Supporting Information

Experimental Realization of Catalytic CH_4 Hydroxylation Predicted for an Iridium NNC Pincer Complex, Demonstrating Thermal, Protic, and Oxidant Stability

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Experimental Section:

General Considerations: Unless otherwise noted all reactions and manipulations were performed using standard Schlenck techniques (argon) or in an MBruan LABmaster 130 glove box (nitrogen). Ultra high purity argon was used and passed through a column of Drierite. GC-MS analysis was performed on a Shimadzu GC-MS QP5000 (ver. 2) equipped with a cross-linked methyl silicone gum capillary column (DB5) and GS-gaspro column. ^{1}H (400MHz), ^{3}C (100MHz), and ^{19}F NMR (376.5 MHz) spectra were collected on a Varian 400 Mercury plus spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts were referenced using residual protiated solvent. All coupling constants are reported in Hz. ^{19}F NMR chemical shifts were referenced using $CFCl_3$. Chemical shifts were assigned based on NOEDIF, g-COSY, g-HSQC, and g-MHBC or cigar experiments. Mass spectrometric analyses were performed at UCLA and UCR Mass Spectrometry Facility. Elemental analyses were performed by Desert Analytical Laboratory, Inc.; Arizona. X-ray Crystallography data were collected on a Bruker SMART APEX CCD diffractometer.

Materials: $IrCl_3$ (Pressure Chemical), Phenyl Lithium (1.8M in butyl ether, Aldrich) were used as is. All solvents were reagent grade or better. Ether, benzene, pentane, and dichloromethane were dried and degassed by sparging with argon then passing through activated alumina using an mBruan MB-SPS solvent purifier system. 6-Phenyl-4,4'-di-tert-butyl-2,2'-bipyridine was prepared following literature procedures.[1]

X-ray structure determination: Diffraction data was collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The cell parameters were obtained from the least-squares

[1] Lu, W.; Mi, B-X; Chan, M. C. W.; Hui, Z.; Che, C-M.; Zhu, N.; Lee, S-T. *J. Am. Chem. Soc*, **2004**. *126*, 4958.

refinement of the spots (collected 60 frames) using the SMART program. A hemisphere of data was collected up to a resolution of 0.77Å, and the intensity data was processed using the Saint Plus program. All calculations for the structure determination were carried out using the SHELXTL package (version 5.1)[2]. Initial atomic positions were located by direct methods using XS, and the structure was refined by least-squares methods using SHELX. Absorption corrections were applied by using SADABS[3]. Calculated hydrogen positions were input and refined in a riding manner along with the attached carbons.

Synthesis of Ir(NN^{tBu}C)ClEt(C_2H_4) (1-Cl), and Ir(NN^{tBu}C)ClEt($NCCH_3$) (1-Cl-$NCCH_3$). $[Ir(C_2H_4)_2Cl]_2$ (1.03 g, 1.82 mmol) was dissolved in CH_2Cl_2 (25 mL) in a Schlenck bomb[4]. In a separate Schlenck flask, 6-phenyl-4, 4'-di-tert-butyl-2, 2'-bipyridine (1.25 g, 3.63 mmol) was dissolved in CH_2Cl_2 (15 mL). Ethylene was then bubbled through the Ir solution while stirring at –50^{o}C for 5min. Under an ethylene atmosphere the dissolved ligand was transferred (by cannula) over. The flask was then washed with CH_2Cl_2 (15 mL) and transferred over. The red solution was then stirred at –50^{o}C for 15min, then allowed to warm to room temp, and stirred for 16h. During the course of the reaction the bomb was opened periodically to relieve excess ethylene pressure. The solvent was then reduced to 20 mL under reduced pressure[5], and ethylene was then bubbled through for 5min. Acetonitrile (20 mL) was then added and the solution was heated at 50^{o}C for 30min. The solvent was then removed, and the resulting red

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[2] Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

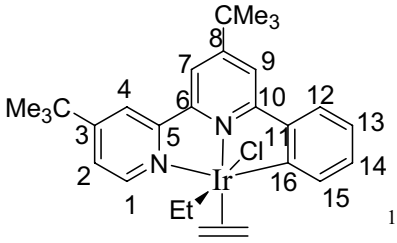
[3] Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

[4] A thick walled glass vessel sealed with a resealable high vacuum PTFE valve.

[5] A minor amount of what is believed to be the cis isomer was also observed, however, this complex is only stable under an ethylene atmosphere. When placed under vacuum the red solution turns slightly greenish. Bubbling ethylene through the solution gives back the red ethylene complex, and after treatment with acetonitrile at 50^{o}C for 30 minutes leads to the trapping and isolation of this side product as the acetonitrile adduct. **1-Cl** can be converted to **1-Cl-$NCCH_3$** by heating in acetonitrile.

residue was passed through neutral alumina with CH_2Cl_2 until the yellow band came off, then ethyl acetate/methanol gradient to remove **1-Cl** (orange band) and acetonitrile complex **1-Cl-NCCH$_3$** (red band). Complexes **1-Cl** and **1-Cl-NCCH$_3$** were obtained as crystalline material by recrystalization from CH_2Cl_2/Pentane at –25°C. Yielding 1.32 g (57.9%) of **1-Cl** and 301.5 mg (13%) of **1-Cl-NCCH$_3$**.

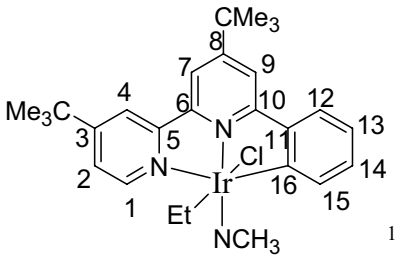
Data for **1-Cl**: ESI-MS: 593.2 $(M - Cl)^+$, 565.2 $(M –Cl -C_2H_4)^+$. Anal. Calc. for $C_{28}H_{36}ClIrN_2$: C 53.53; H 5.78; N 4.46, Cl 5.64; Found: C 53.44, H 5.67, N 4.39, Cl 5.59.



^{1}H NMR of **1-Cl**[6]: δ 9.21 (d, 1H, ^3J = 6.1, H-1), 8.04 (d, 1H, ^4J = 2.0, H-4), 7.94 (d, 1H, ^4J = 1.6, H-9), 7.80 (d, 1H, ^4J = 1.6, H-7), 7.73 (dd, 1H, ^3J = 8.0 ^4J = 1.0, H-15), 7.68 (dd, 1H, ^3J = 7.8 ^4J = 1.6, H-12), 7.56 (dd, 1H, ^3J = 6.1 ^4J = 2.1, H-2), 7.28 (dt, 1H, ^3J = 7.5 ^4J = 1.6, H-14), 7.13 (dt, 1H, ^3J = 7.5 ^4J = 1.0, H-13), 3.97 (s, 4H, C_2H_4), 1.52 (s, 9H, CMe_3), 1.48 (s, 9H, CMe_3), 0.47 (dq, 1H, ^2J = 10.8 ^3J = 7.7, -**CH$_2$**-), 0.25 (dq, 1H, ^2J = 10.8 ^3J = 7.7, -**CH$_2$**-), -0.28 (t, 3H, ^3J = 7.7, $-CH_3$). $^{13}C\{^1H\}$ NMR: δ 163.88(C-8), 163.04(C-3), 162.28(C-16), 158.40(C-5), 153.18(C-6), 151.21(C-1), 144.76(C-11), 144.38(C-10), 134.99(C-15), 131.67(C-14), 124.90(C-12), 124.63(C-2), 122.74(C-13), 119.61(C-4), 116.17(C-9), 115.13(C-7), 65.86(C_2H_4), 35.59(**C**Me_3), 35.47(**C**Me_3), 30.94(C**Me**$_3$), 30.62(C**Me**$_3$), 14.95(-**CH$_3$**), -7.52(-**CH$_2$**-).

[6] The ethylene resonances at 3.88 ppm (4H), are coincidently chemical equivalent and appear as a singlet instead of the expected multiplet for the C_s symmetry. However, in acetic acid-d_4 (DOAc), the ethylene resonances at 3.95 ppm are a multiplet.

Data for **1-Cl-NCCH$_3$**: ESI-MS: 647.2(M-Cl +NCCH$_3$)$^+$ 606.2 (M-Cl)$^+$, 565.2 (M-Cl-NCCH$_3$)$^+$. Anal. Calc. for $C_{27}H_{35}ClIrN_3$: C 52.44, H 5.50, N, 6.55, Cl 5.53; Found: C 52.03, H 5.47, N 6.23, Cl 5.62.



^{1}H NMR of **1-Cl-NCCH$_3$:** δ 8.78 (d, 1H, ^3J = 5.7, H-1), 7.91 (d, 1H, ^4J = 1.8, H-4), 7.66 (d, 1H, ^4J = 1.6, H-9), 7.61 (d, 1H, ^4J = 1.6, H-7), 7.55 (m, 2H, H-12, 15), 7.48 (dd, 1H, ^3J = 5.7 ^4J = 1.8, H-2), 7.14 (dt, 1H, ^3J = 7.7, 7.3, ^4J = 1.4, H-14), 6.98 (dt, 1H, ^3J = 7.6, 7.4, ^4J = 1.3, H-13), 2.69 (s, 3H, NCCH$_3$), 1.44 (s, 9H, CMe$_3$), 1.43 (s, 9H, CMe$_3$), 0.91 (m, 1H, -**CH$_2$**-), 0.67 (m, 1H, -**CH$_2$**-), 0.21 (t, 1H, ^3J = 7.7, -**CH$_3$**). ^{13}C{^{1}H} NMR: δ 167.79(C-16), 161.83(C-3), 160.88(C-8), 157.64(C-5), 155.59(C-6), 154.08(C-10), 149.98(C-1), 145.21(C-11), 133.67(C-15), 130.99(C-14), 124.90(C-12), 124.12(C-2), 120.75(C-13), 119.32(C-4), 115.07(N**C**CH$_3$), 114.82(C-9), 114.06(C-7), 35.38(**C**Me$_3$), 31.07(**C**Me$_3$), 30.74(C**Me**$_3$), 16.05(-**CH$_3$**), 5.07(NC**CH$_3$**), -9.47(-**CH$_2$**-).

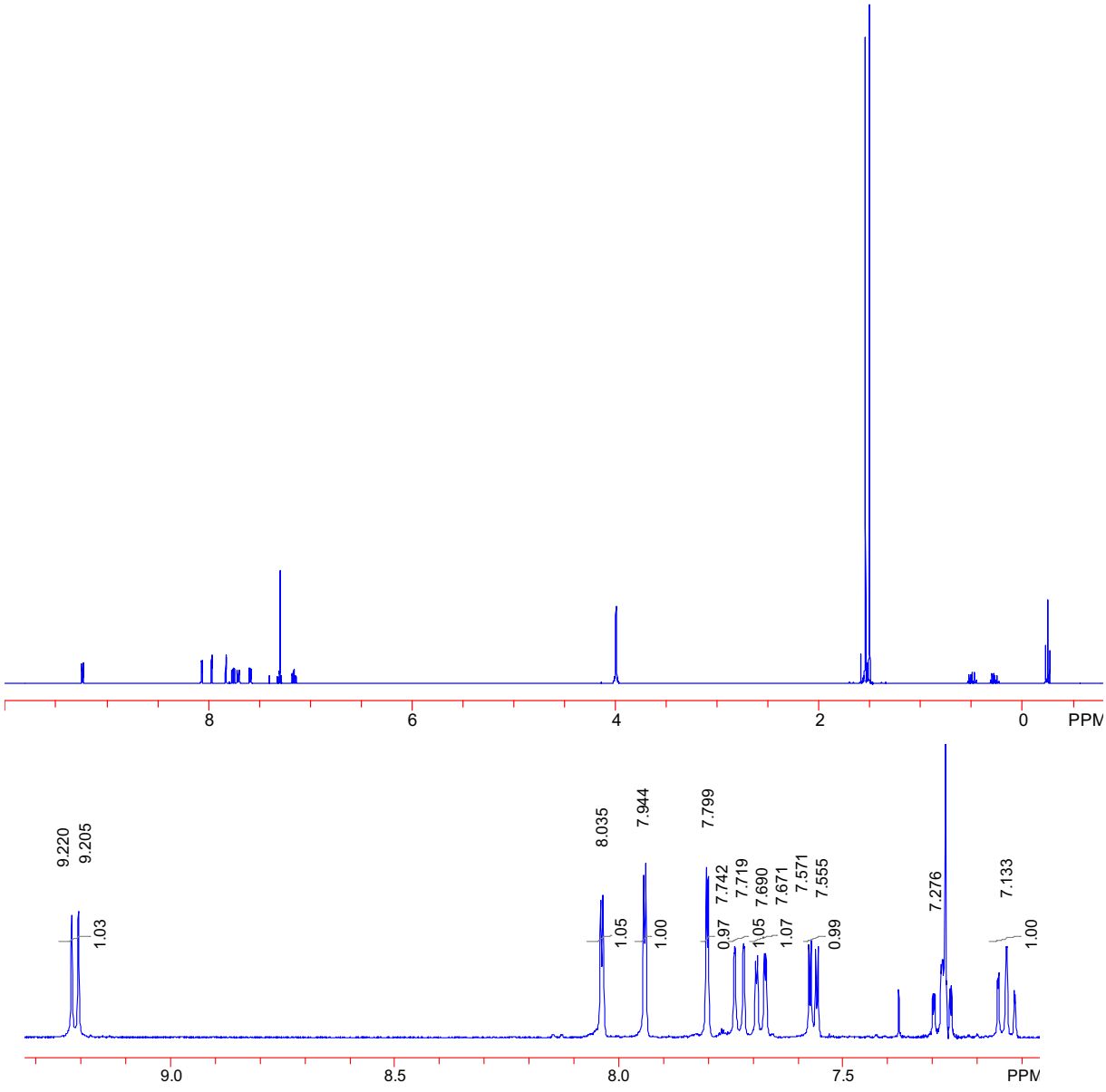


Figure S1. ^{1}H NMR spectra of 1-Cl, top) full spectra, bottom) expansion of aromatic region.

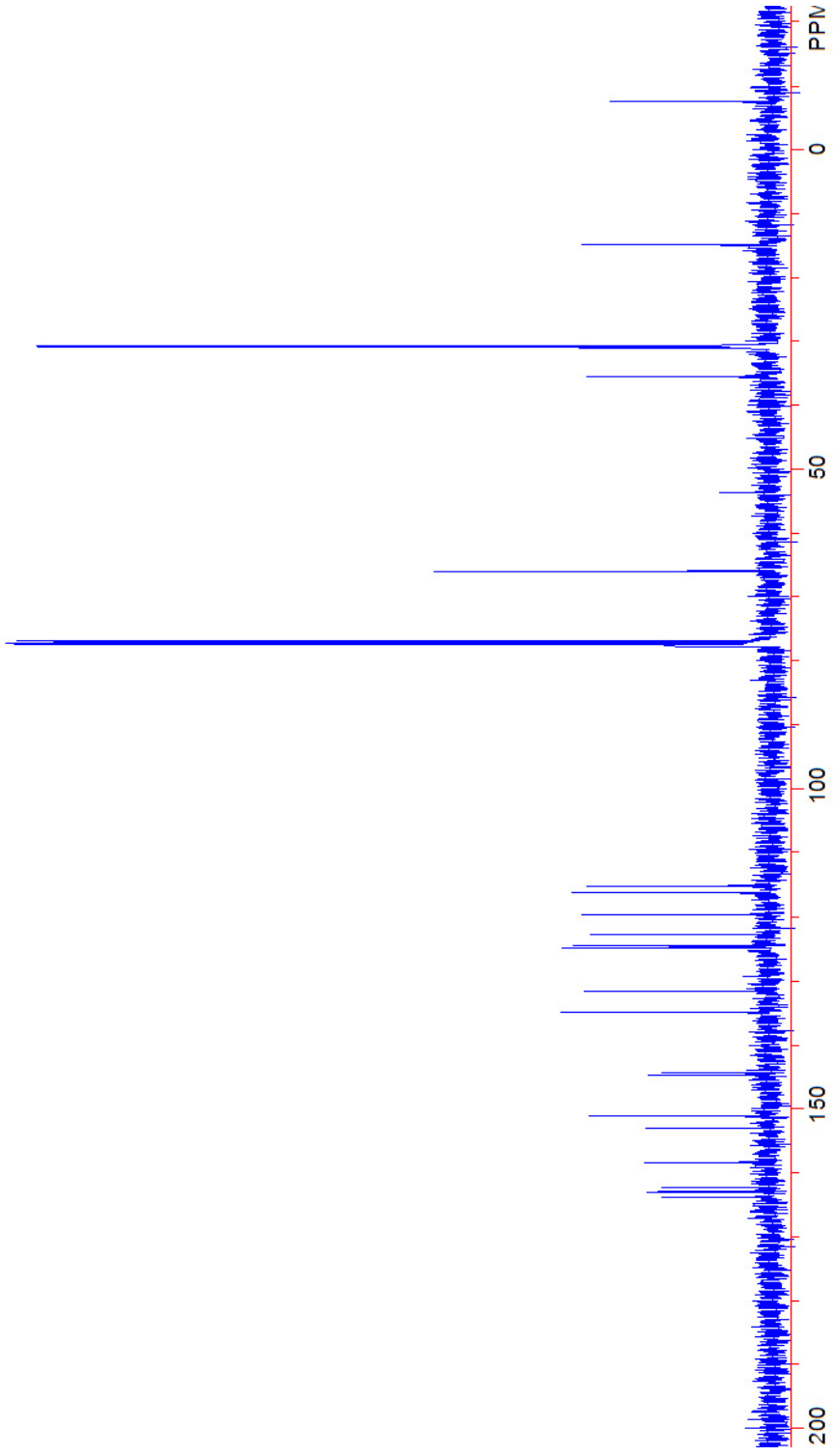


Figure S2. ^{13}C NMR spectra of 1-Cl.

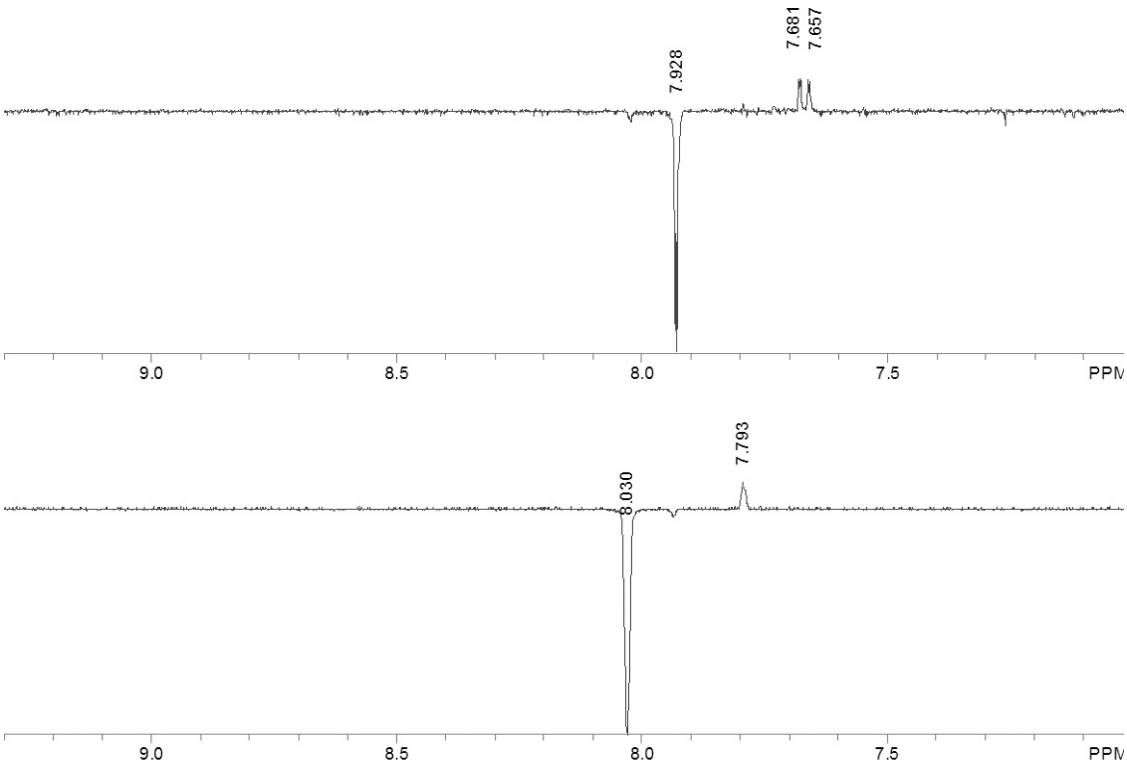


Figure S3. NOEDIFF experiment of 1-Cl.

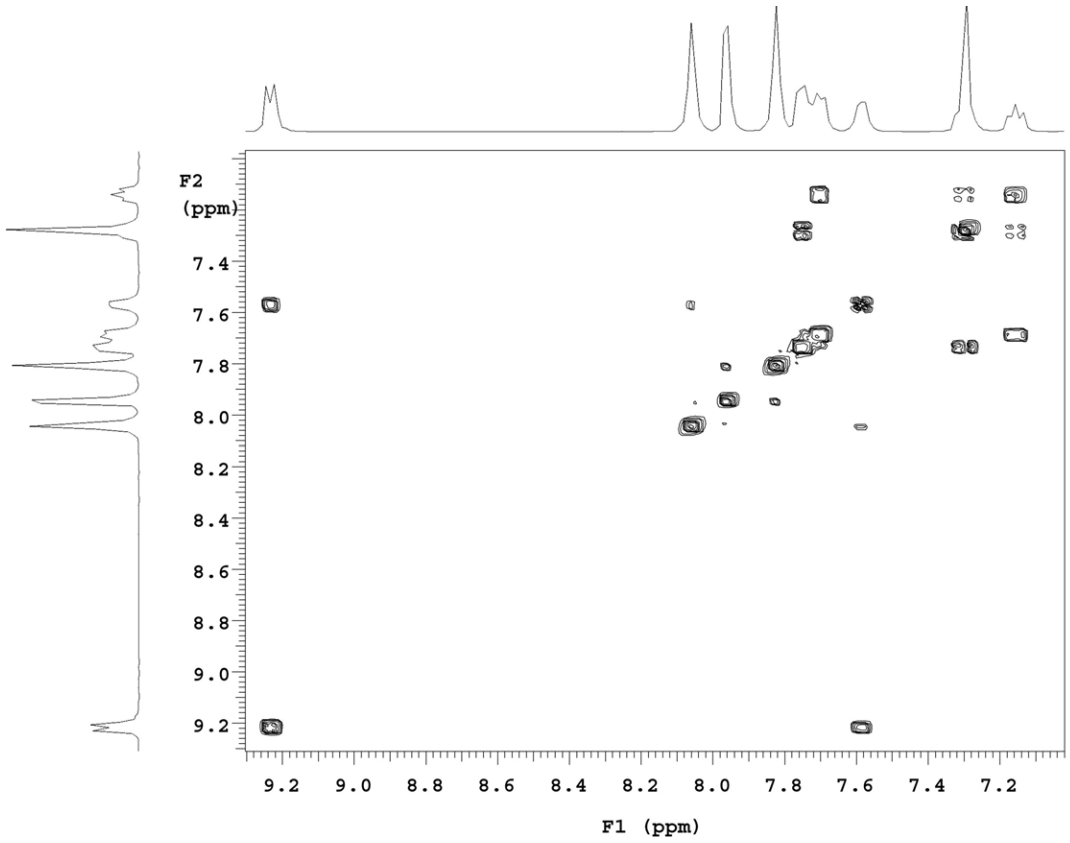


Figure S4. g-COSY experiment of 1-Cl (expansion of aromatic region).

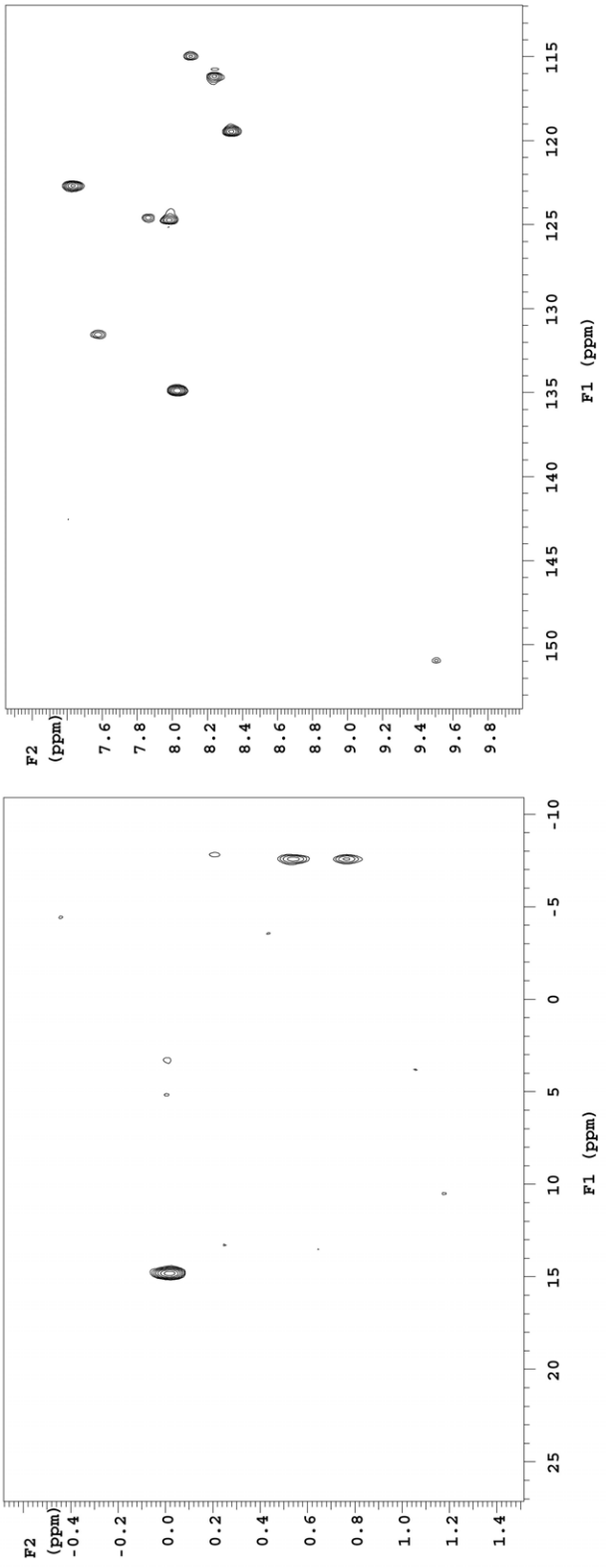


Figure S5. g-HSQC experiment of 1-Cl, top) aromatic region, bottom) aliphatic region.

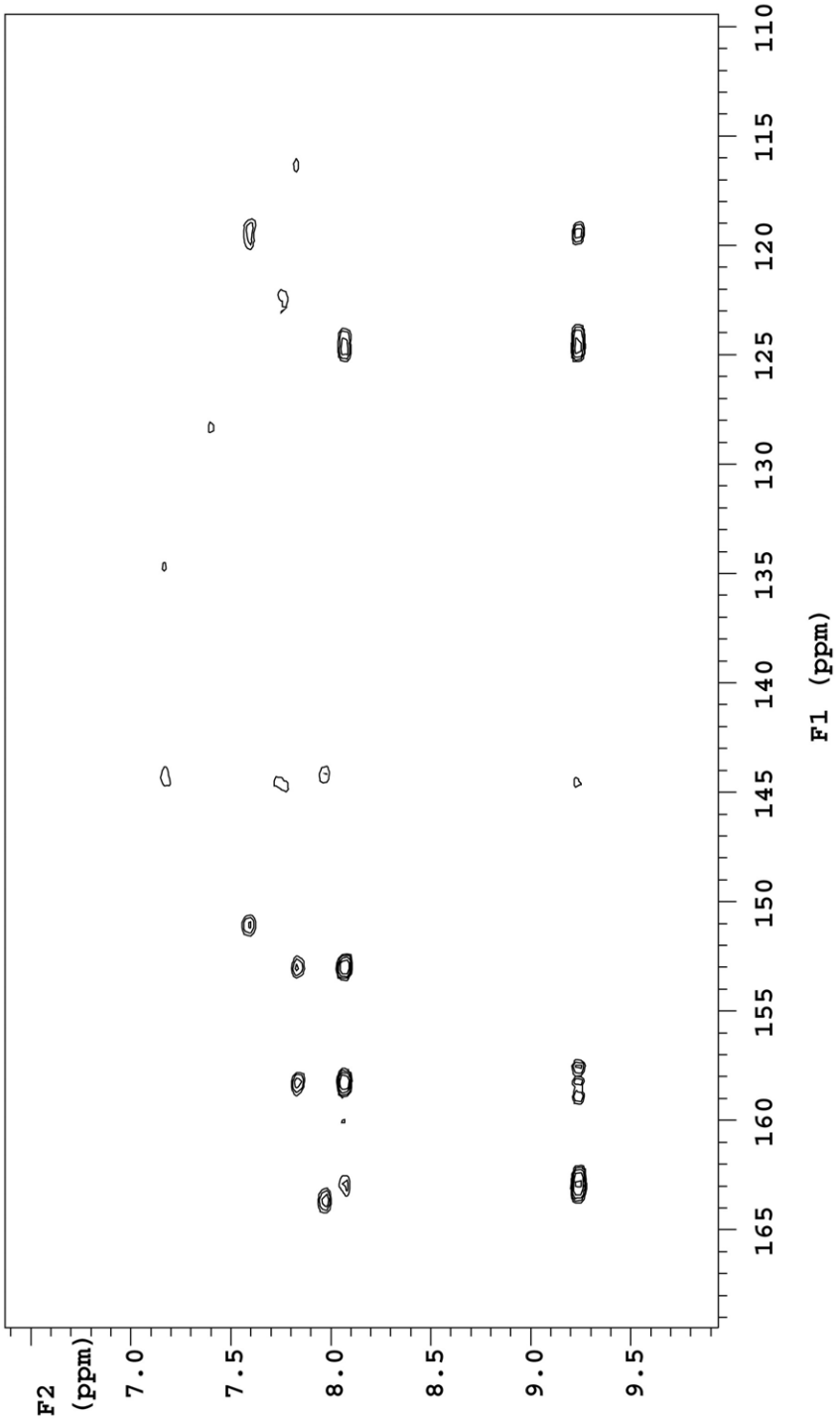


Figure S6. CIGAR (^{1}H-^{13}C correlation) experiment of 1-Cl (expansion of aromatic region).

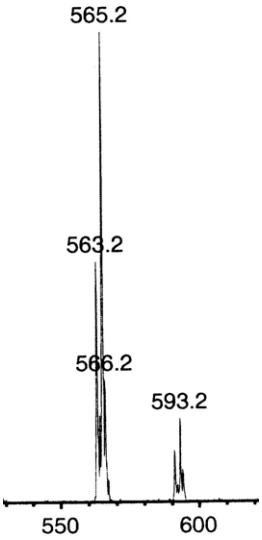


Figure S7. ESI-MS of 1-Cl.

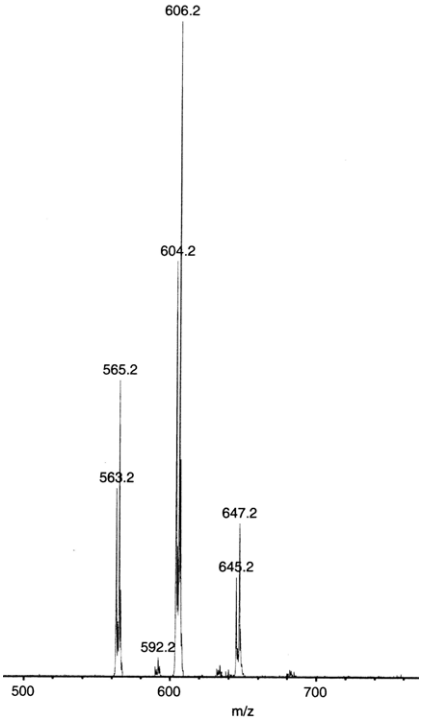


Figure S8. ESI-MS of 1-Cl-$NCCH_3$.

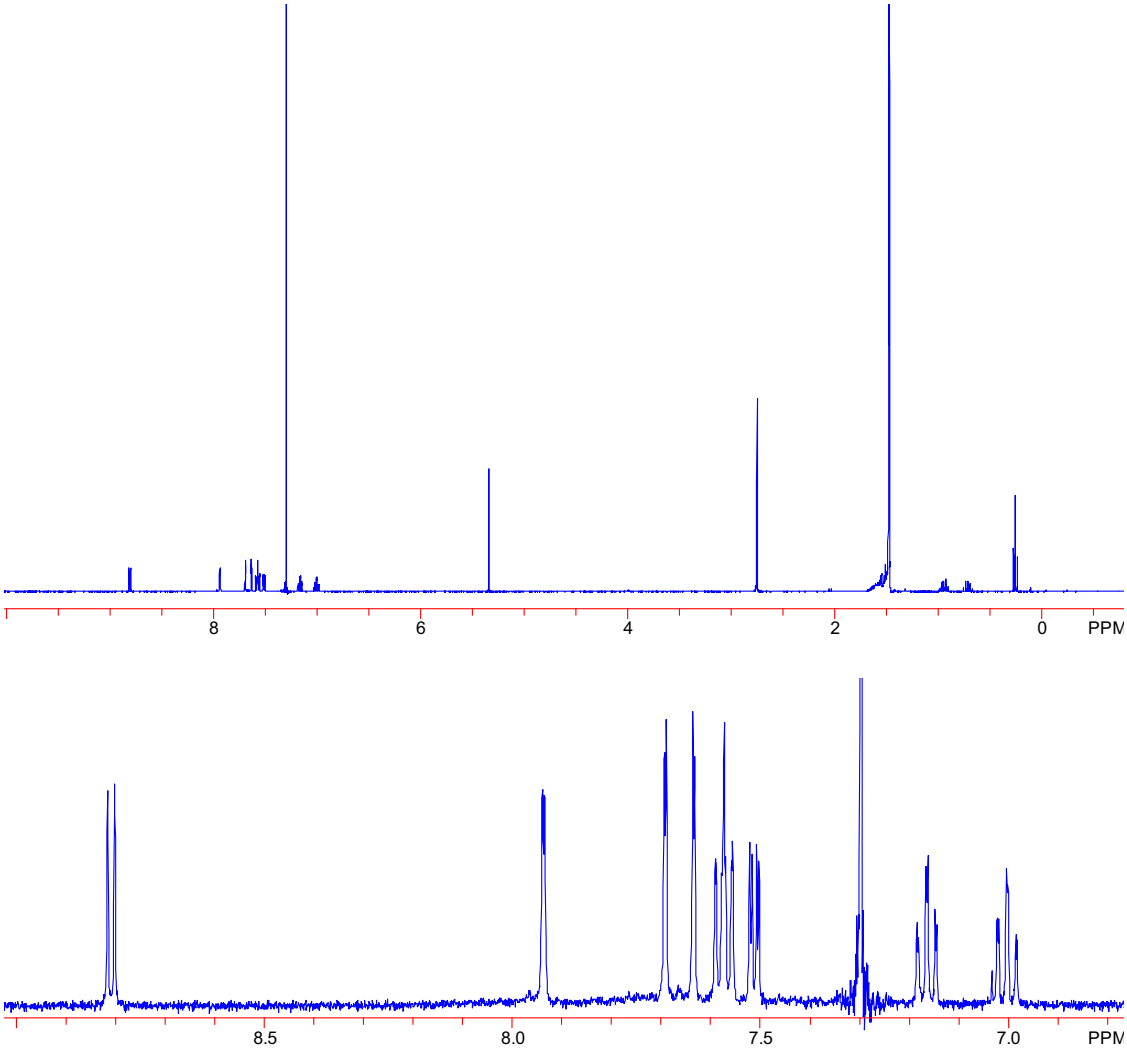


Figure S9. ^{1}H NMR of 1-Cl-NCCH$_3$, top) full spectra, bottom) expansion of aromatic region region.

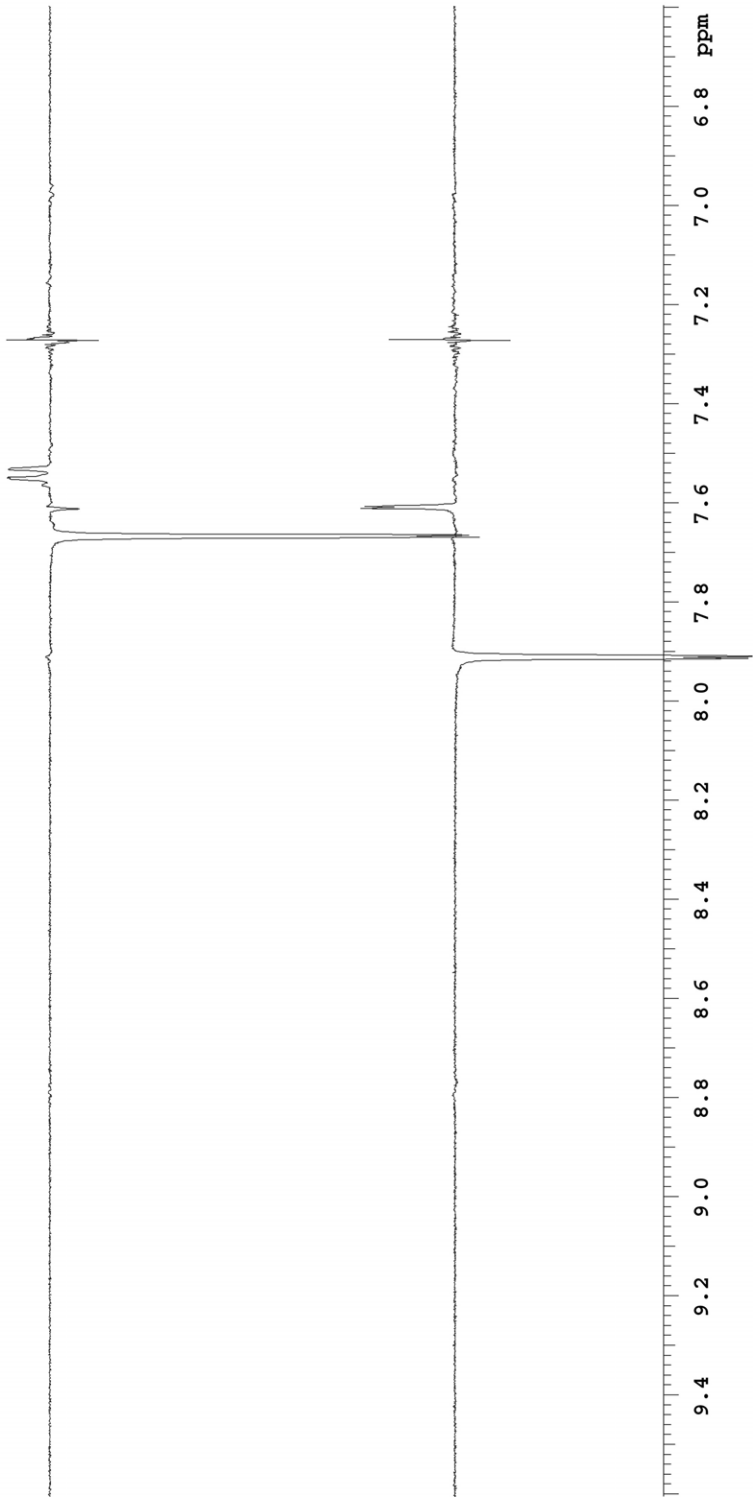


Figure S10. NOEDIFF experiment of 1-Cl-$NCCH_3$.

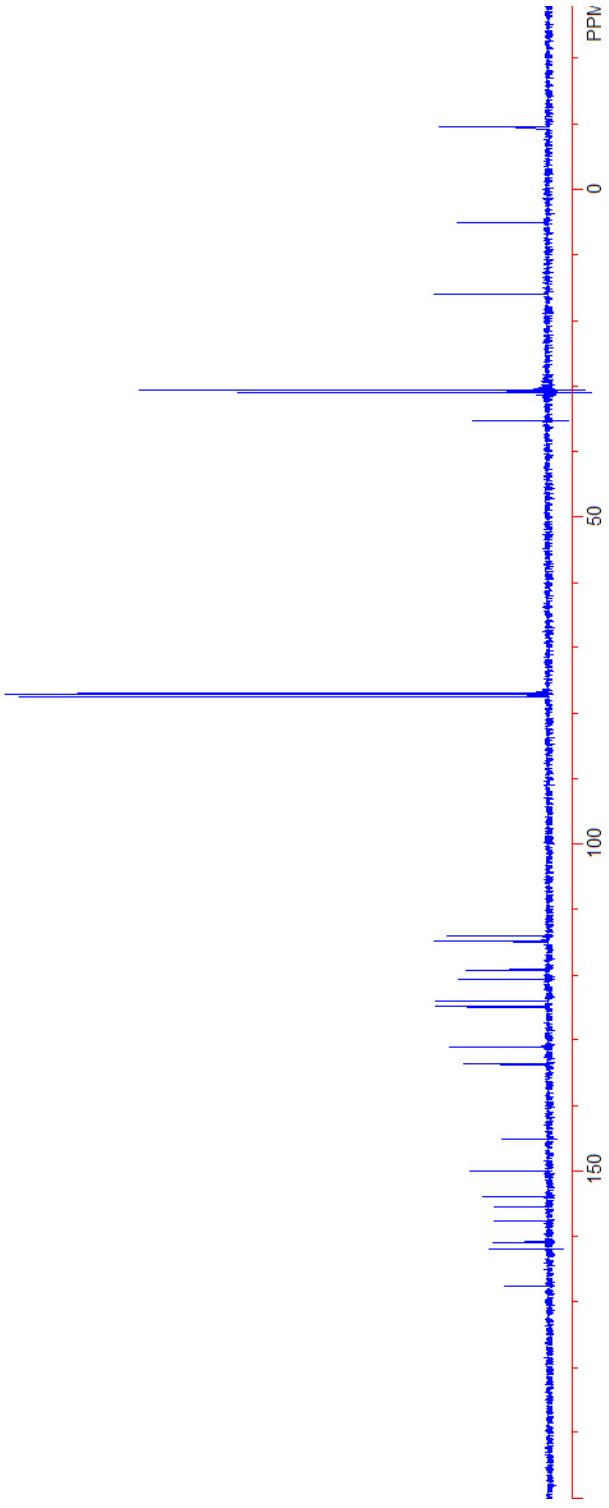


Figure S11. ^{13}C NMR of 1-Cl-$NCCH_3$.

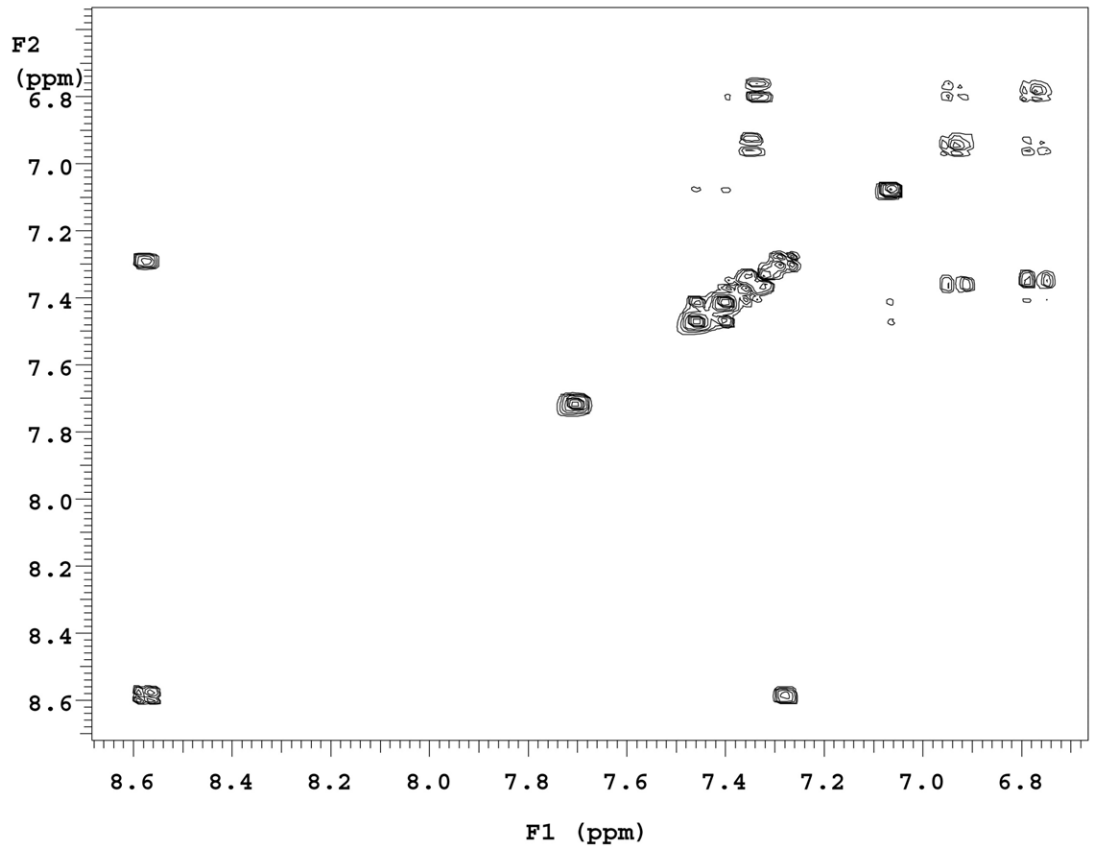


Figure S12. g-COSY of 1-Cl-NCCH$_3$.

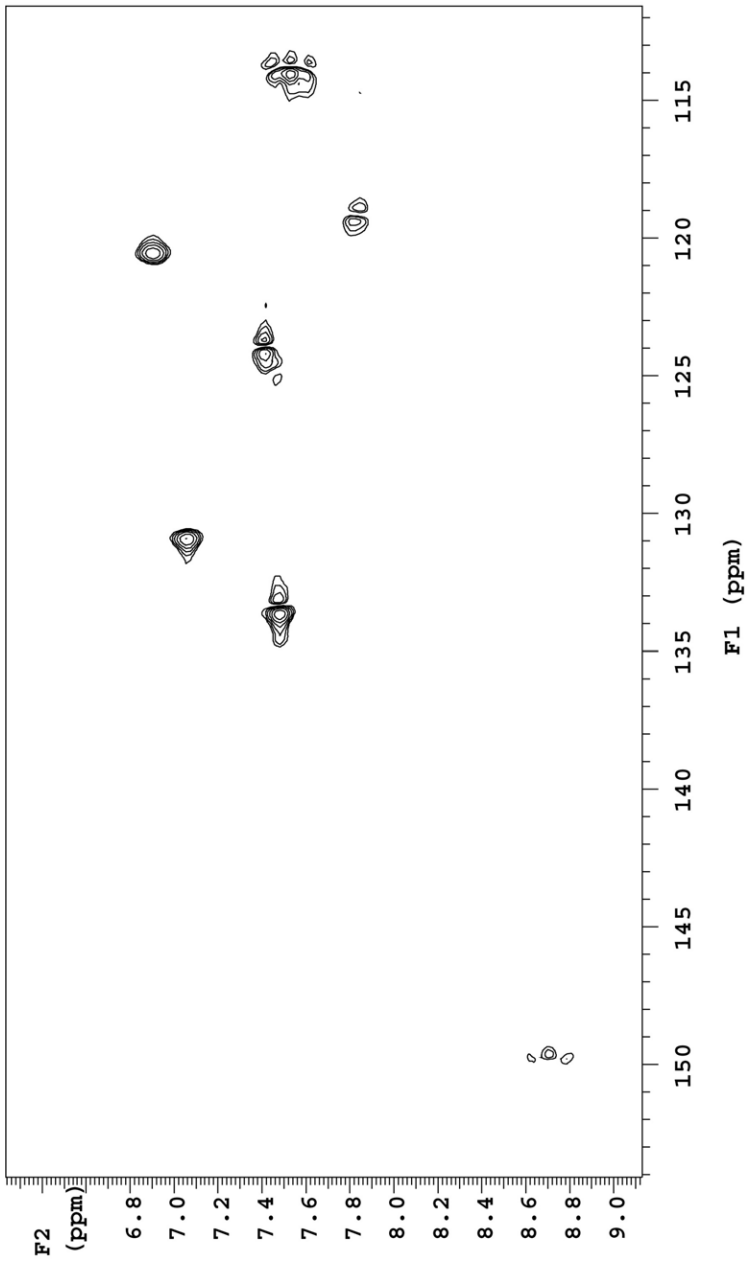


Figure S13. g-HMQC (^{1}H-^{13}C correlation) experiment of 1-Cl-$NCCH_3$ (expansion of aromatic region).

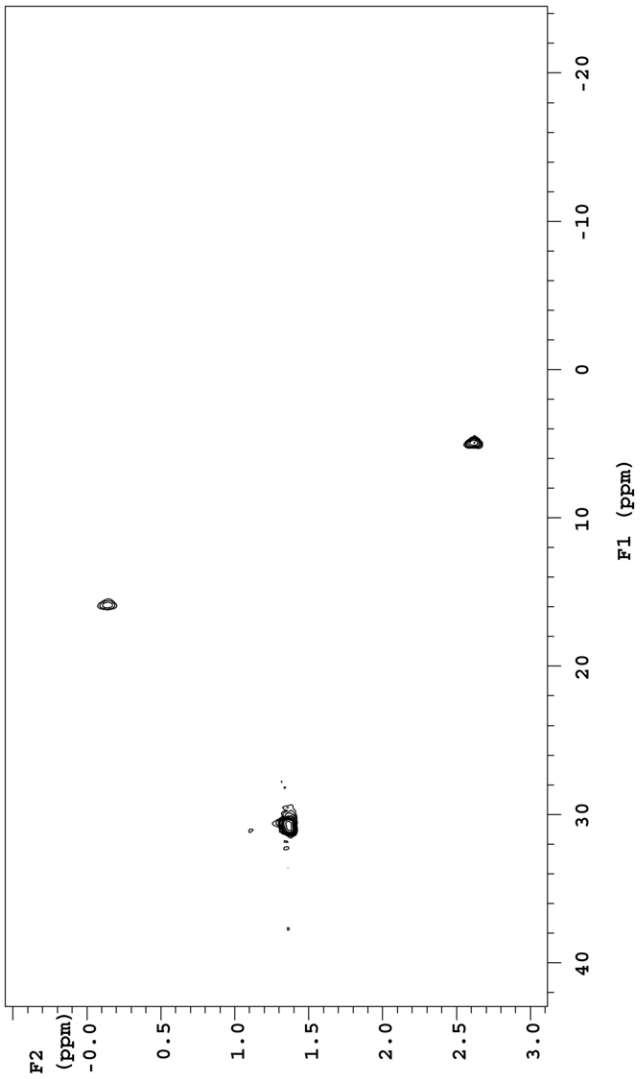


Figure S14. g-HMQC (^{1}H-^{13}C correlation) experiment of 1-Cl-NCCH$_3$ (expansion of aliphatic region).

X-ray structure determination of 1-Cl. Suitable orange-yellow crystals of **1-Cl** were grown from a CH_2Cl_2/pentane mixture at –20^{o}C. Diffraction data was collected at 133K. The thermal ellipsoid plot is shown in Figure S16. There are 2 molecules in the unit cell and it co-crystallized with a CH_2Cl_2 solvent molecule. Crystal data and refinement parameters can be found in Table 5. Selected bond lengths and angles can be found in Table 7.

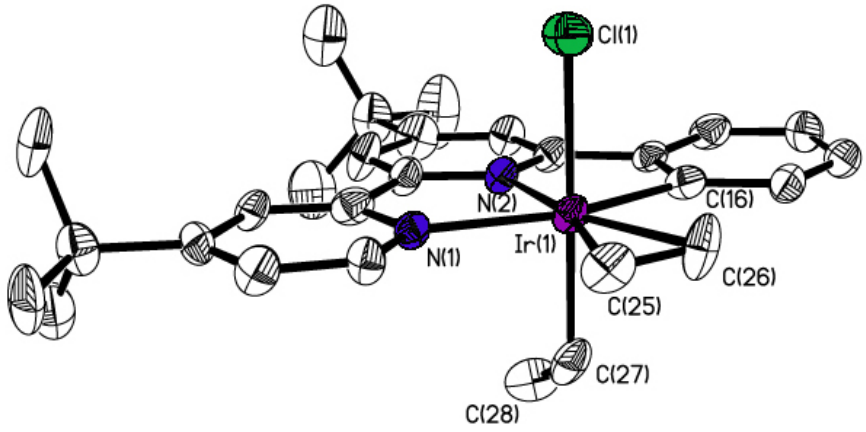


Figure S16. Thermal ellipsoids plot of **1-Cl** with 50% probability. Hydrogen's, and CH_2Cl_2 co-solvent removed for clarity.

Synthesis of Ir(NN^{tBu}C)TFAEt(C_2H_4) (1-TFA). Complex **1-Cl** (376 mg, 0.599 mmol) and silver trifluoroacetate (169 mg, 0.659 mmol) were stirred at room temperature in CH_2Cl_2 (15 mL) in the dark for 1 day. The resulting suspension was filtered over celite, and the filtrate was collected. Orange-yellow microcrystalline material was obtained from a CH_2Cl_2/pentane solution at –25°C. Yield 427.7 mg (96.2%). Anal. Calc. for $C_{30}H_{36}F_3IrN_2O_2$: C 51.05; H 5.14; F 8.07; N 3.97; Found C 50.75; H 4.98; F 8.14; N 3.96.

^{1}H NMR: δ 9.20 (d, 1H, ^3J = 6.2, H-1), 8.034 (d, 1H, ^4J = 2.1, H-4), 7.93 (d, 1H, ^4J = 1.6, H-9), 7.81 (d, 1H, ^4J = 1.6, H-7), 7.71 (d, 1H, ^3J = 8.0, H-15), 7.68 (dd, 1H, ^3J = 7.7 ^4J = 1.6, H-12), 7.56 (dd, 1H, ^3J = 6.1 ^4J = 2.1, H-2), 7.28 (dt, 1H, ^3J = 7.8, 7.5, H-14), 7.16 (t, 1H, ^3J = 7.7, 7.4, H-13), 3.95 -3.85 (m, 4H, C_2H_4), 1.53 (s, 9H, CMe_3), 1.48 (s, 9H, CMe_3), 0.47 (m, 1H, ^3J = 10.5, 7.7, -CH_2-), 0.27 (dq, 1H, ^3J = 10.5, 7.7, -CH_2-), -0.38 (t, 3H, ^3J = 7.7, -CH_3). ^{13}C{^{1}H} NMR: δ 164.08(C-16), 163.39(C-3), 162.69(C-8), 159.49(C-5), 154.37(C-6), 151.39(C-1), 145.14(C-10), 143.39(C-11), 135.34(C-15), 131.48(C-14), 124.75(C-12), 124.50(C-2), 123.17(C-13), 119.29(C-4), 116.03(C-9), 115.04(C-7), 66.28(C_2H_4), 35.71(**C**Me_3), 35.59(**C**Me_3), 30.98(C**Me**$_3$), 30.66(C**Me**$_3$), 15.10(-**CH_3**), -14.68(-**CH_2**-). ^{19}F NMR: δ –75.87.

X-ray structure determination of 1-TFA. Suitable crystals of **1-TFA** were grown by vapor diffusion of pentane in to a C_6H_6 solution. Diffraction data were collected at 143(2) K. It co-crystallized with a C_6H_6 solvent molecule. Crystal data and refinement parameters can be found in Table 10. Selected bond lengths and angles can be found in Table 12. Final structure refinement for ($C_{33}H_{30}F_3IrN_2O_4$) results in a R_{int} = 5.3 %, R_1 = 5.4 % and wR_2 = 12.2 %.

We located an obvious normal case of positional disorder in the ethyl group located axially relative to the NNC ligand's plane. A second Q peak were located and assigned a corresponding label to its component. A second FVAR card was added; the site occupancy factors (sof) of part 1 were changed to one times the second free variable and the sof of part 2 were changed to one minus the value of the second free variable. For more clear imaging geometrical restraint SADI were applied to obtain the target distance and angle (1.40 Å for C29 – C30 / C30a, and 120^o for Ir1 – C29 – C30 / C30a). Also located in the asymmetric unit cell is one half a solvent benzene molecule. The complete benzene molecule can be generated by a SHELX grow function or by defining the symmetry equivalent atom operation by use of an EQIV_$1 card. For aesthetic purposes target bond lengths and angles (1.35 Å sp2 C – C and 120^o C31 – C32 – C33) bonds are restrained by DFIX cards.

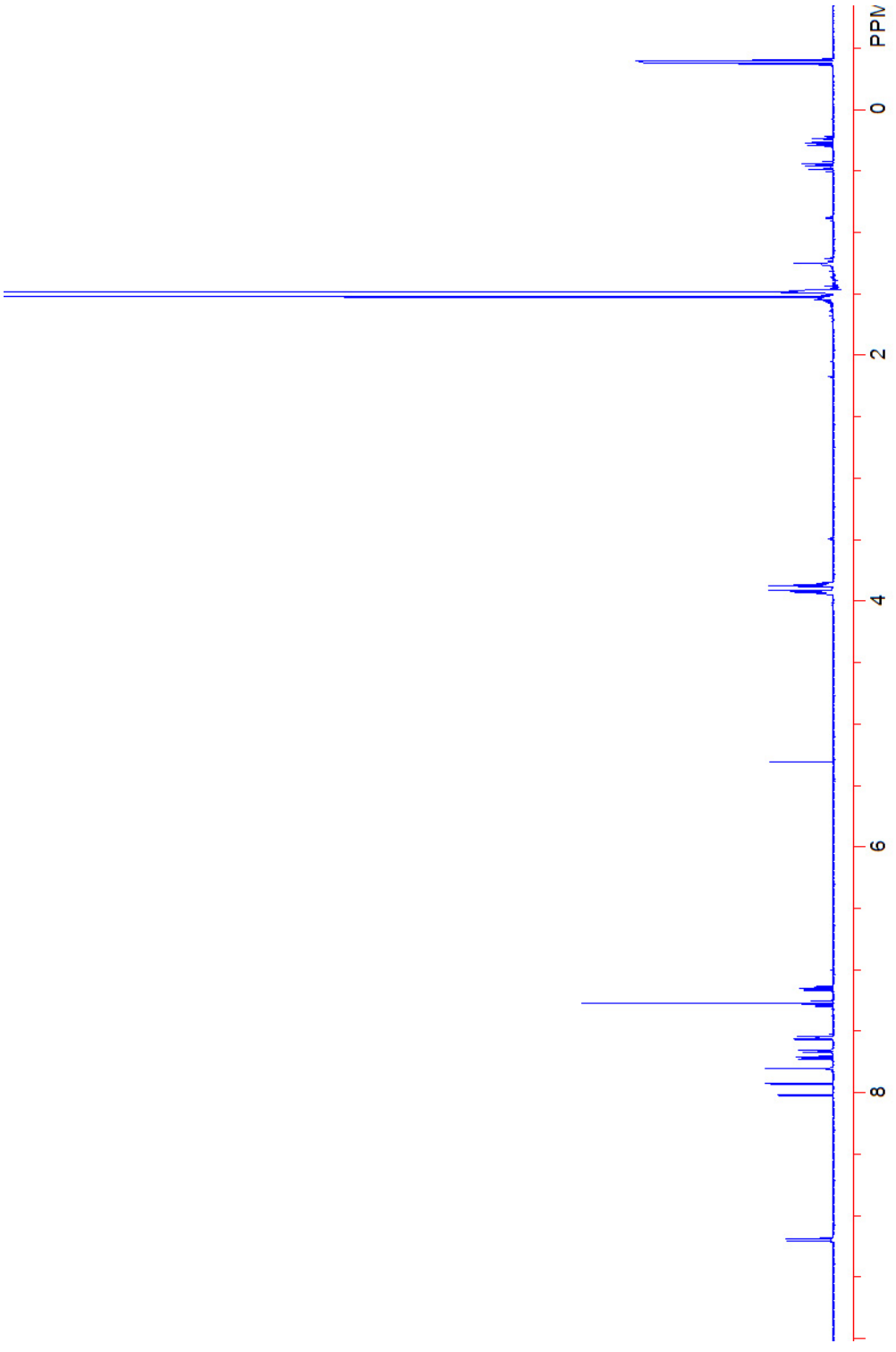


Figure S17. ^{1}H NMR of 1-TFA.

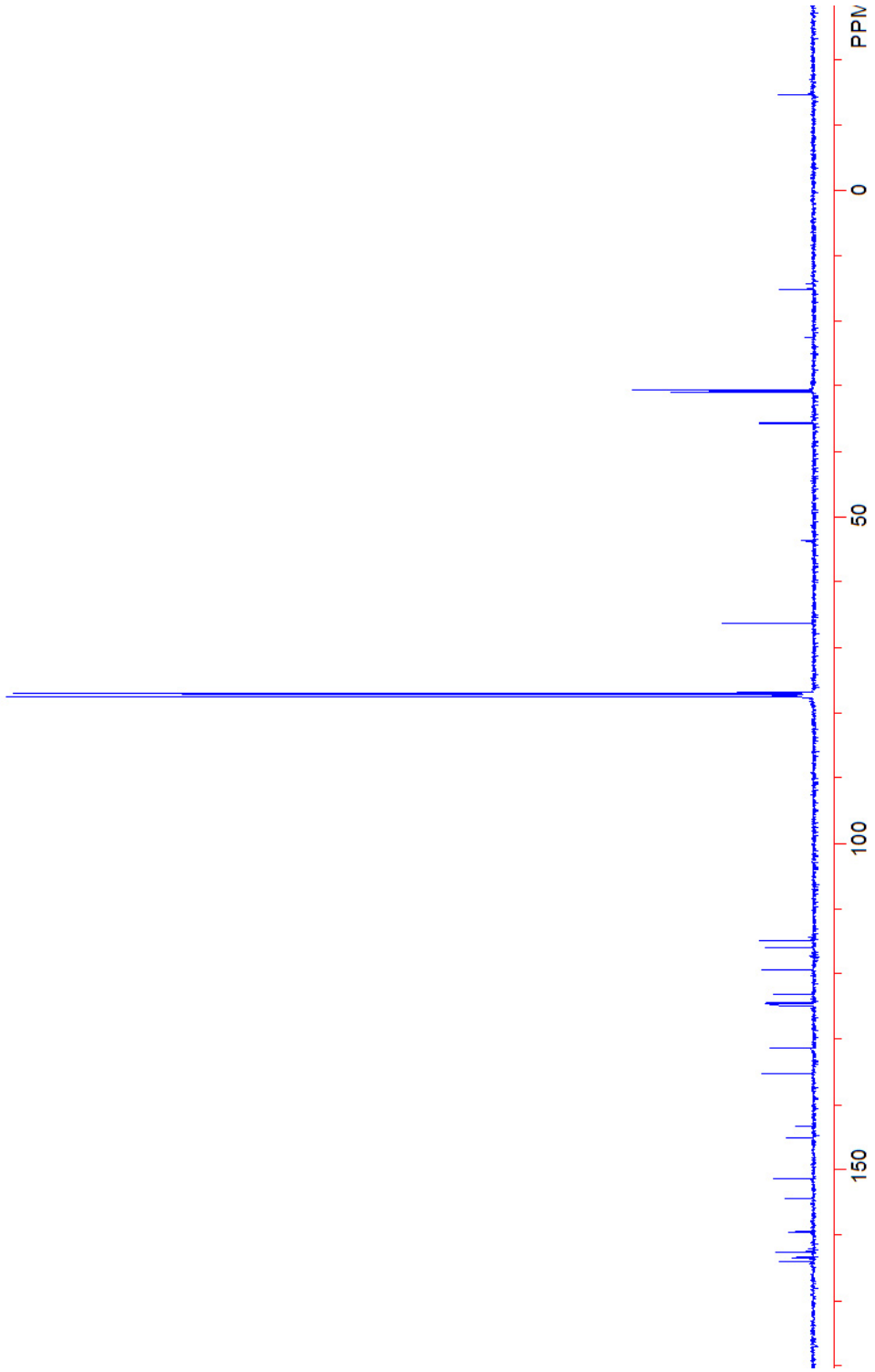


Figure S18. ^{13}C NMR of 1-TFA.

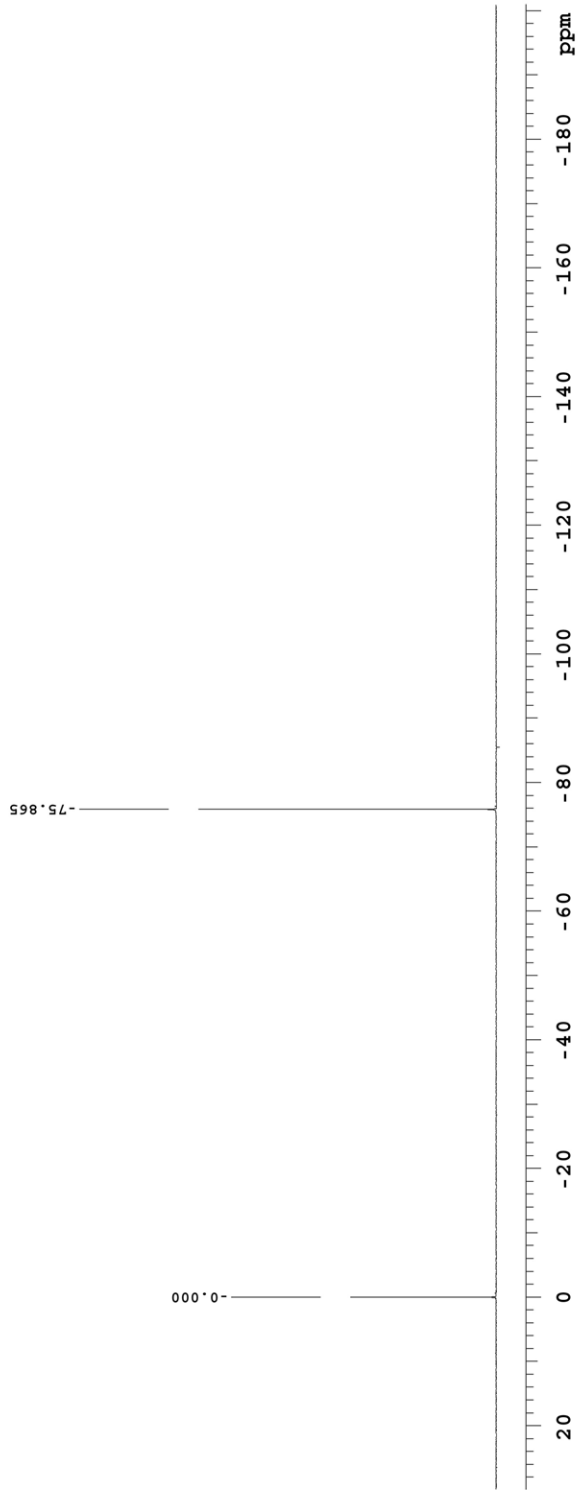


Figure S19. ^{19}F NMR of 1-TFA.

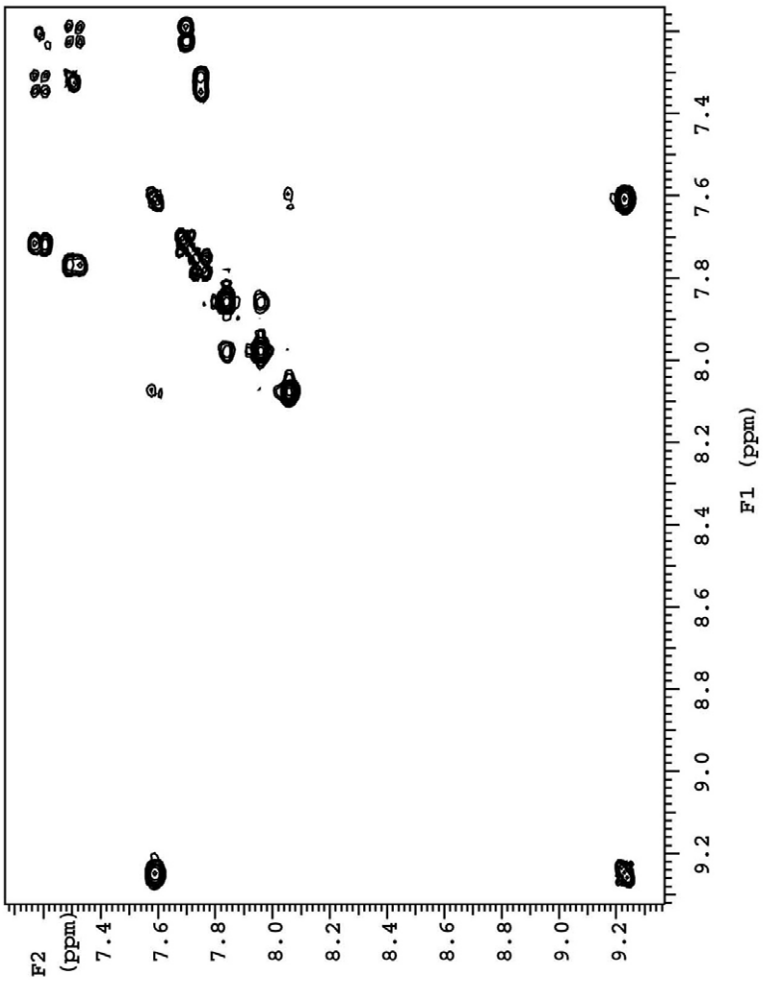


Figure S20. g-COSY NMR of 1-TFA.

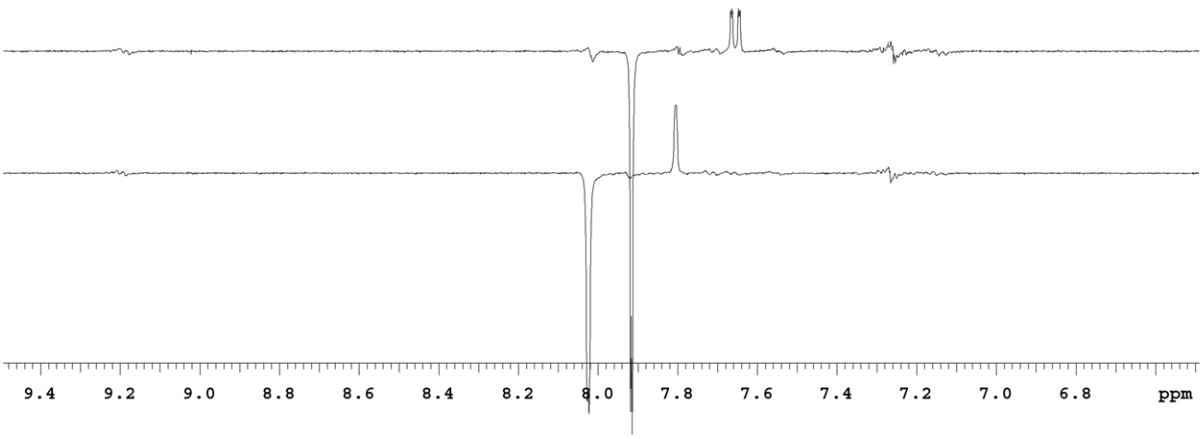


Figure S21. NOEDIF spectra of 1-TFA.

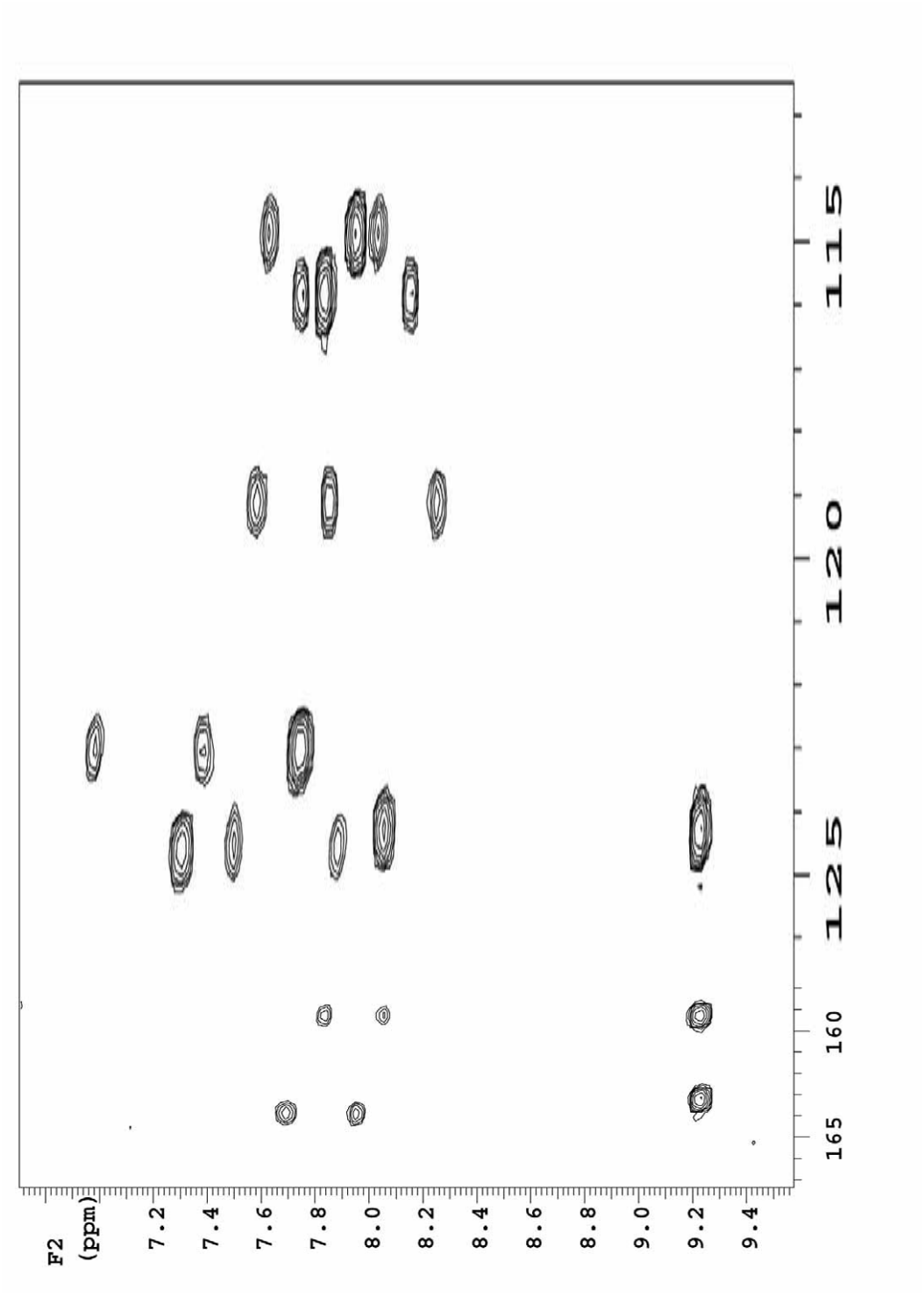


Figure S22. g-HMBC spectra of 1-TFA.

Synthesis of Ir(NN^{tBu}C)TFA$_2$(C$_2$H$_4$). Complex **1-TFA** (552 mg, 0.7815 mmol) was dissolved in neat HTFA (15 mL) under argon and stirred overnight at RT. The solvent was

removed under vacuum. The resulting residue was passed through alumina with CH_2Cl_2 to remove (NNC)Ir(TFA)$_2$(C_2H_4)**,** then THF to remove an unassigned 2nd band, then EtOAc/MeOH to remove the solvent complex[7]. Yield 281.5 mg (45.6%).

Data for **1-TFA$_2$:** HRESI-MS calc for $C_{30}H_{31}F_6IrN_2NaO_4$: 813.1715 $(M+Na)^+$, found 813.1714 (-0.1ppm). Anal. Calc. for $C_{30}H_{31}F_6IrN_2O_4 \cdot H_2O$: C 44.61; H 4.12; N 3.47, found C 44.73, H 4.06, N 3.46.

^{1}H NMR: 9.28 (d, 1H, ^{3}J = 6.2, H-1), 8.11(d, 1H, ^{4}J = 2.2, H-4), 7.99(d, 1H, ^{4}J = 1.9, H-9), 7.90(d, 1H, ^{4}J = 1.8, H-7), 7.77(d, 1H, ^{3}J = 8.1, H-15), 7.71(dd, 1H, ^{3}J = 7.7, 4J =1.3, H-12), 7.66(d, 1H, ^{3}J =6.1, 4J = 2.2, H-2), 7.36(dt, 1H, ^{3}J = 7.9, ^{4}J = 1.67, H-14), 7.20(t, 1H, ^{3}J = 7.7, ^{4}J = 2.2, H-13), 4.84(s, 4H, C_2H_4), 1.55(s, 9H, CMe_3), 1.49(s, 9H, CMe_3). ^{13}C NMR: 164.74, 164.68, 164.38(J_{C-F} = 37.1), 160.36, 155.96, 151.73, 146.41, 135.81, 132.18, 131.48, 125.08, 124.97, 124.74, 119.64, 116.48, 115.78, 111.8(J_{C-F} = 290.8), 72.68, 35.77, 35.65, 30.94, 30.58. ^{19}F NMR: -75.61.

Data for **1-TFA$_2$H$_2$O:** HRESI-MS calc for $C_{28}H_{28}N_2O_4F_6Ir$: 763.1583 $(M-H_2O+H)^+$, found 763.1583. Anal. Calc. for $C_{28}H_{27}F_6IrN_2O_4 \cdot H_2O$: C 43.13; H 3.75; N 3.59, found[8] C 43.62, H 3.77, N 3.47.

^{1}H NMR: 9.10(s, 2H, H_2O), 8.99(d, 1H, ^{3}J = 5.7, H1), 8.06(d, 1H, ^{4}J = 1.7, H-4), 7.75(dd, 1H, ^{3}J = 5.7, ^{4}J = 1.8Hz, H-2), 7.73(m, 3H, H-7,9,15), 7.57(dd, 1H, ^{3}J = 7.7, ^{4}J = 1.4, H12), 7.26(dt, 1H, ^{3}J = 7.7, ^{4}J = 1.2, H-14), 7.06(dt, 1H, ^{3}J = 7.5, ^{4}J = 1.2, H-13), 1.53(s, 9H, CMe_3), 1.51(s, 9H, CMe_3). ^{13}C NMR: 170.31, 169.14(J_{C-F} = 38.1), 164.54, 164.48, 157.62, 157.25, 150.26,

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[7] The solvent complex is believed to be initially made but upon passing through the column the HTFA is replaced with H_2O.

[8] Elemental analysis fits better for loss of 0.5 equiv of H_2O Anal. Calc. for $C_{28}H_{27}F_6IrN_2O_4 \cdot 0.5H_2O$: C, 43.63; H, 3.66; N, 3.63, found[8] C 43.62, H 3.77, N 3.47.

147.12, 139.63, 136.02, 130.90, 125.03, 124.80, 123.59, 119.98, 115.15, 115.04, 112.83(J_{C-F} = 290.4), 35.81, 35.61, 31.23, 30.77. ^{19}F NMR: –75.69.

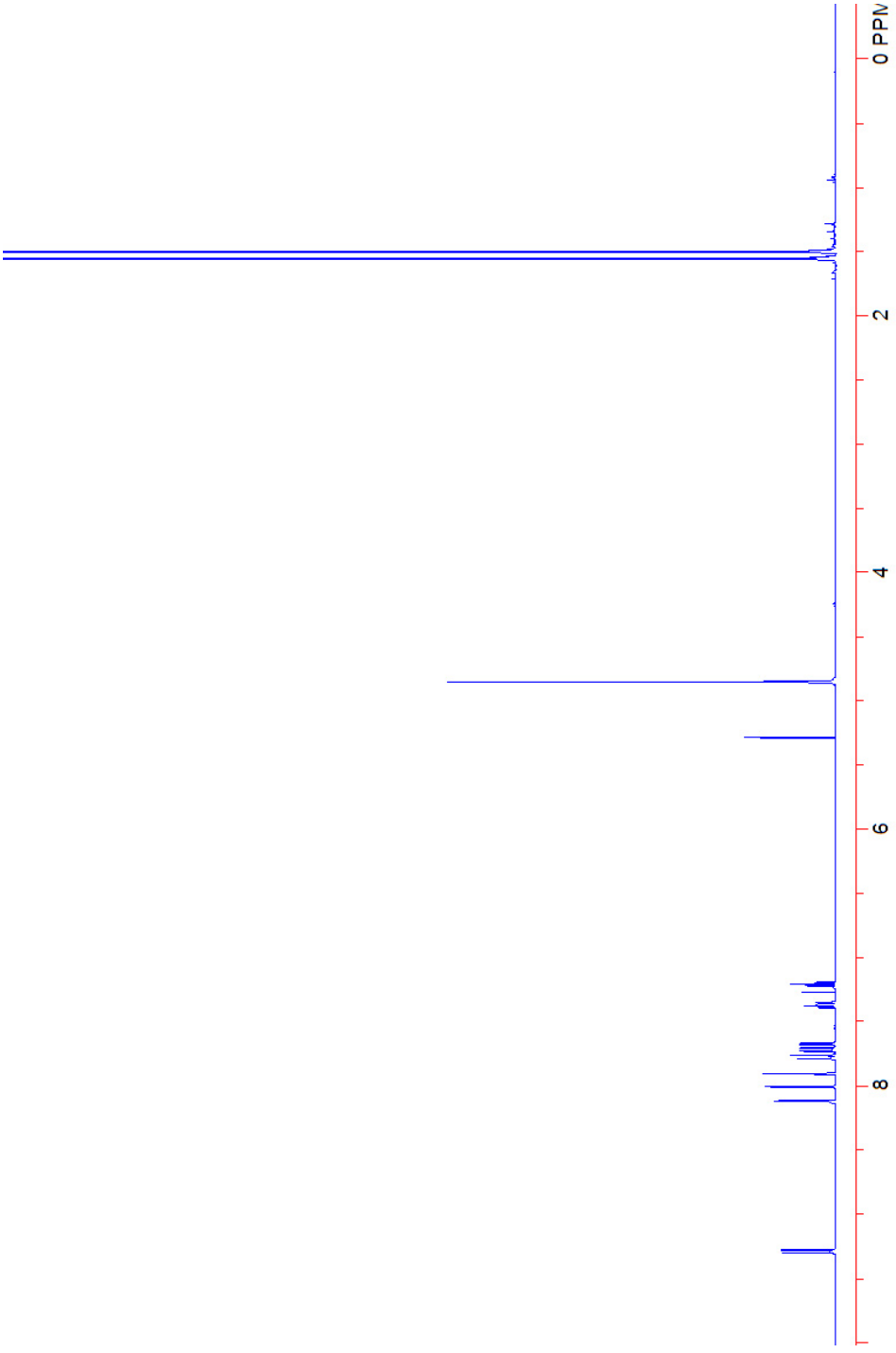


Figure S23. ^{1}H NMR of 1-TFA_2.

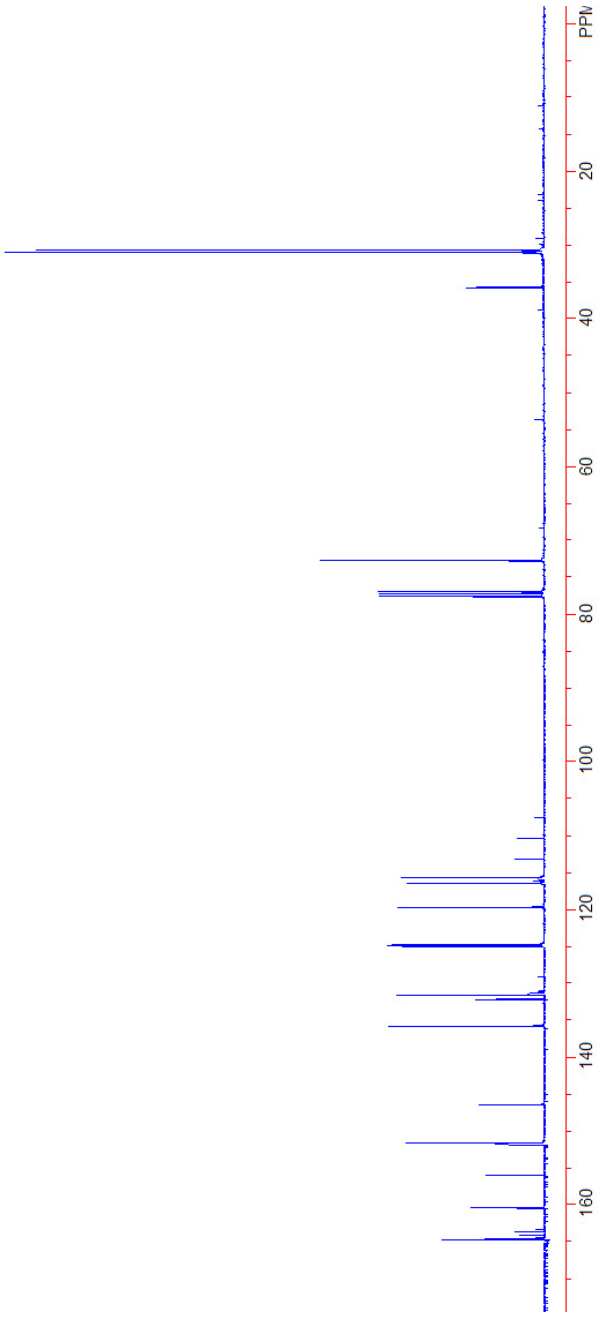


Figure S24. ^{13}C NMR of 1-TFA_2.

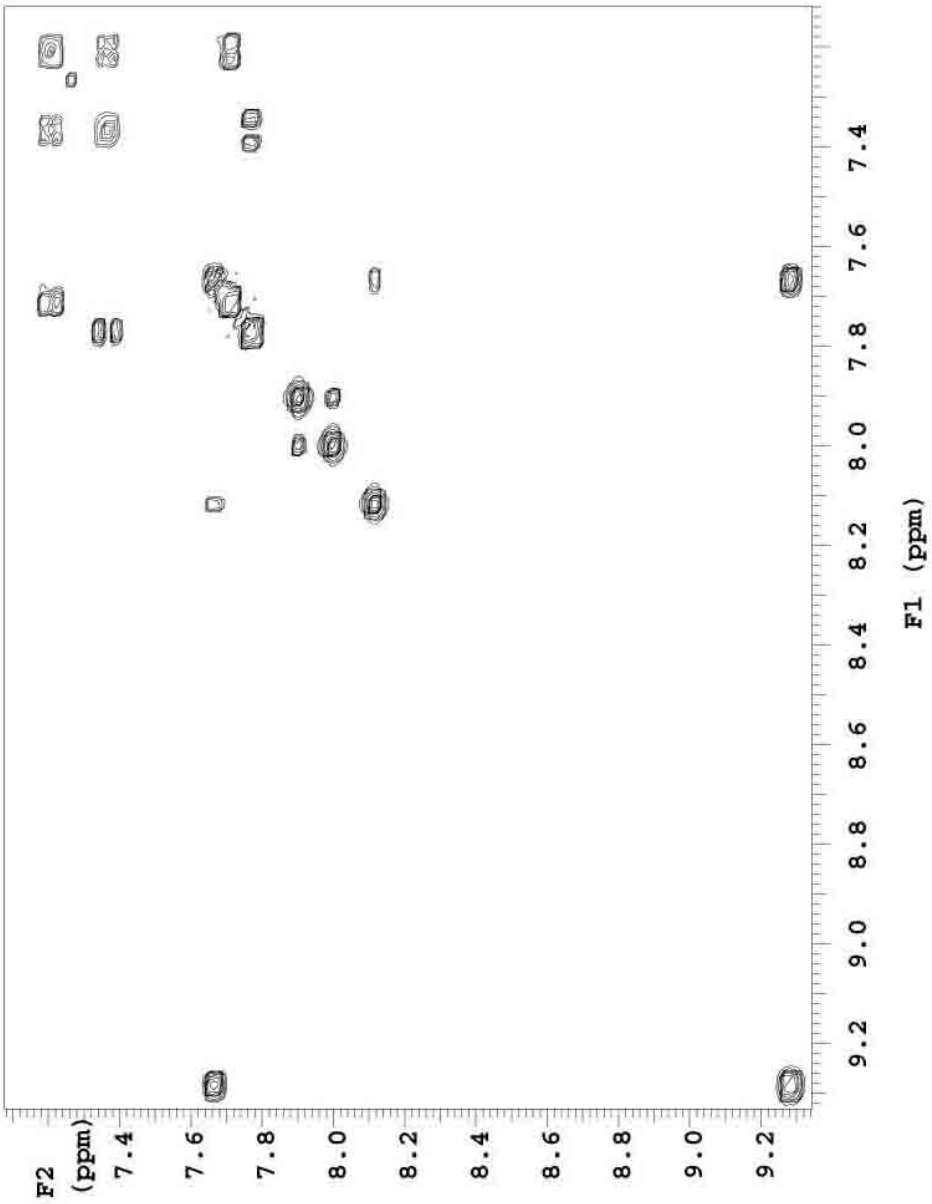


Figure S25. g-COSY of 1-TFA_2.

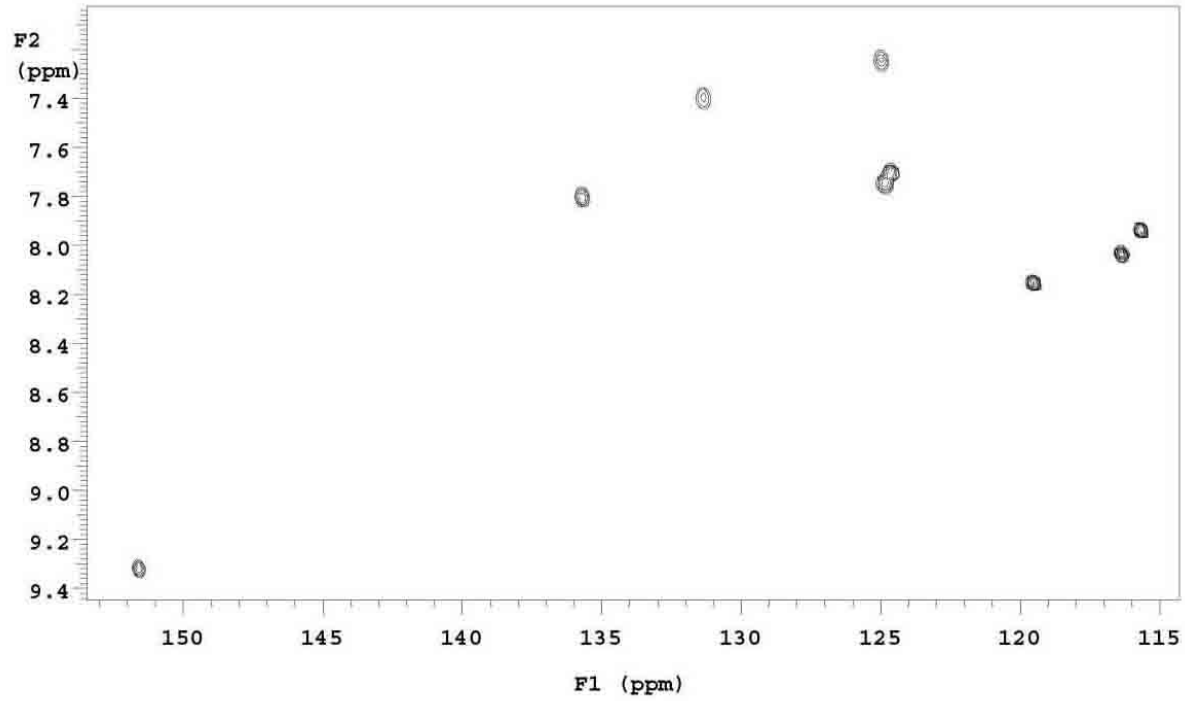


Figure S26. g-HMQC of 1-TFA_2.

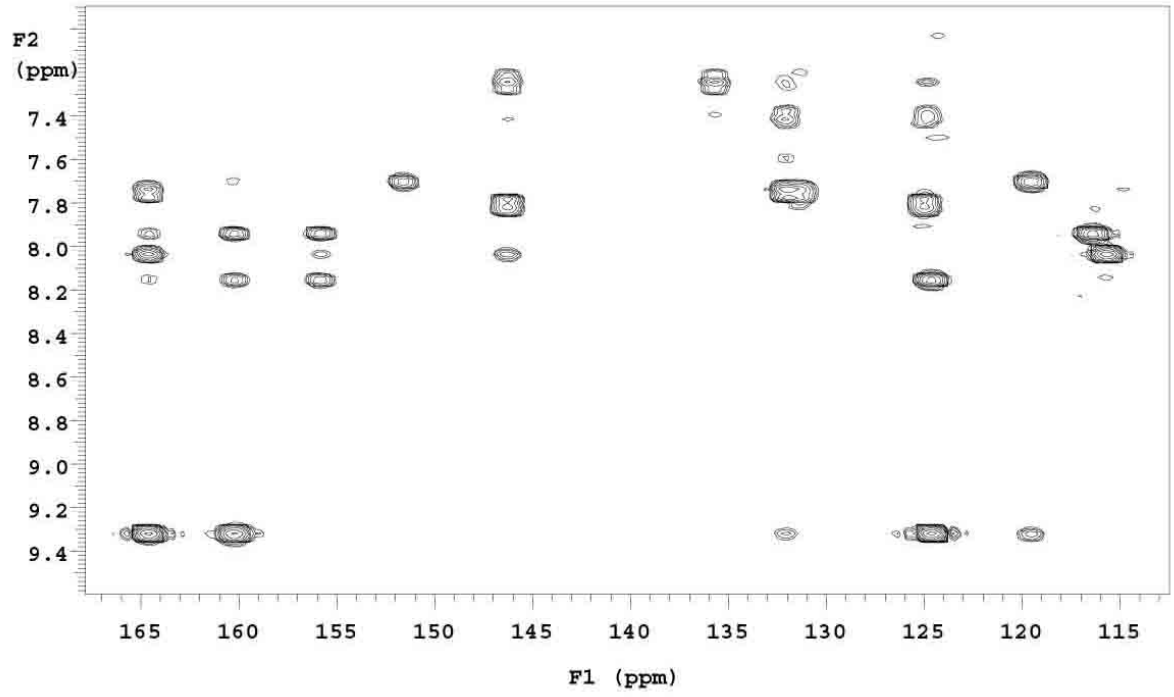
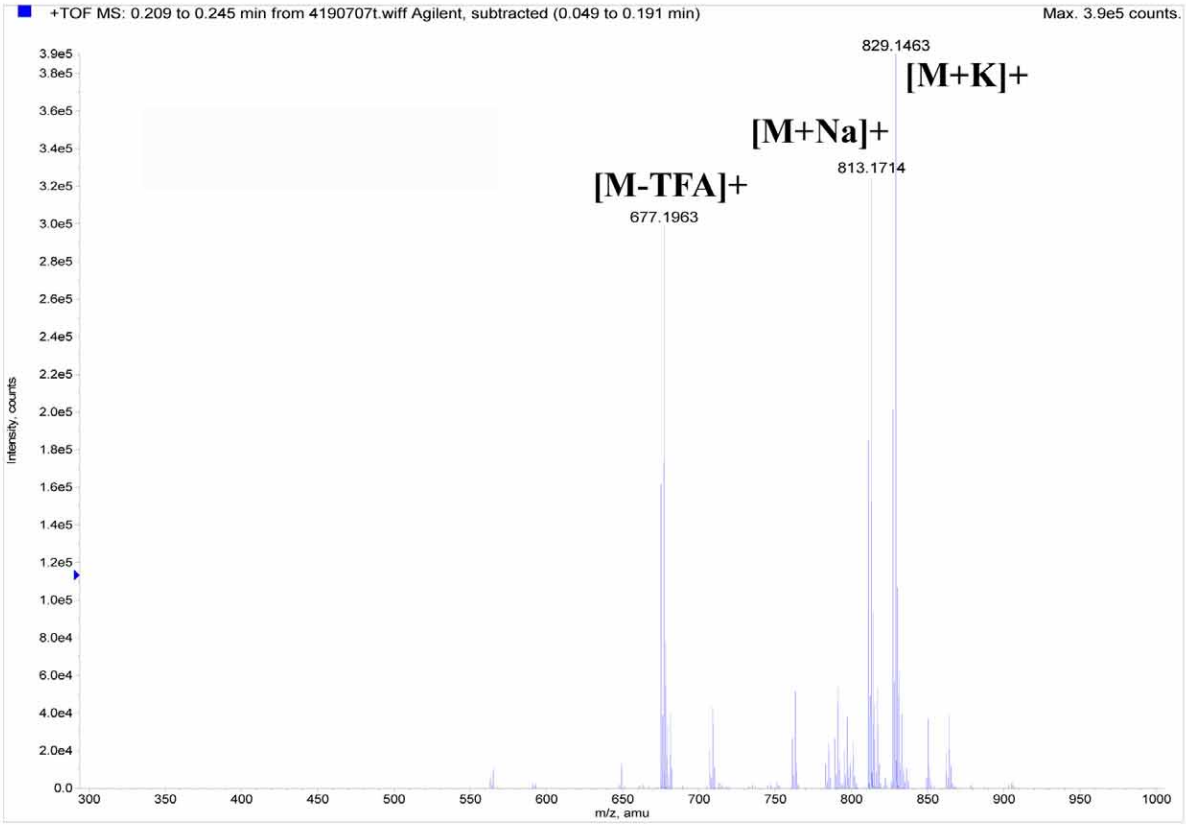


Figure S27. g-HMBC of 1-TFA_2.

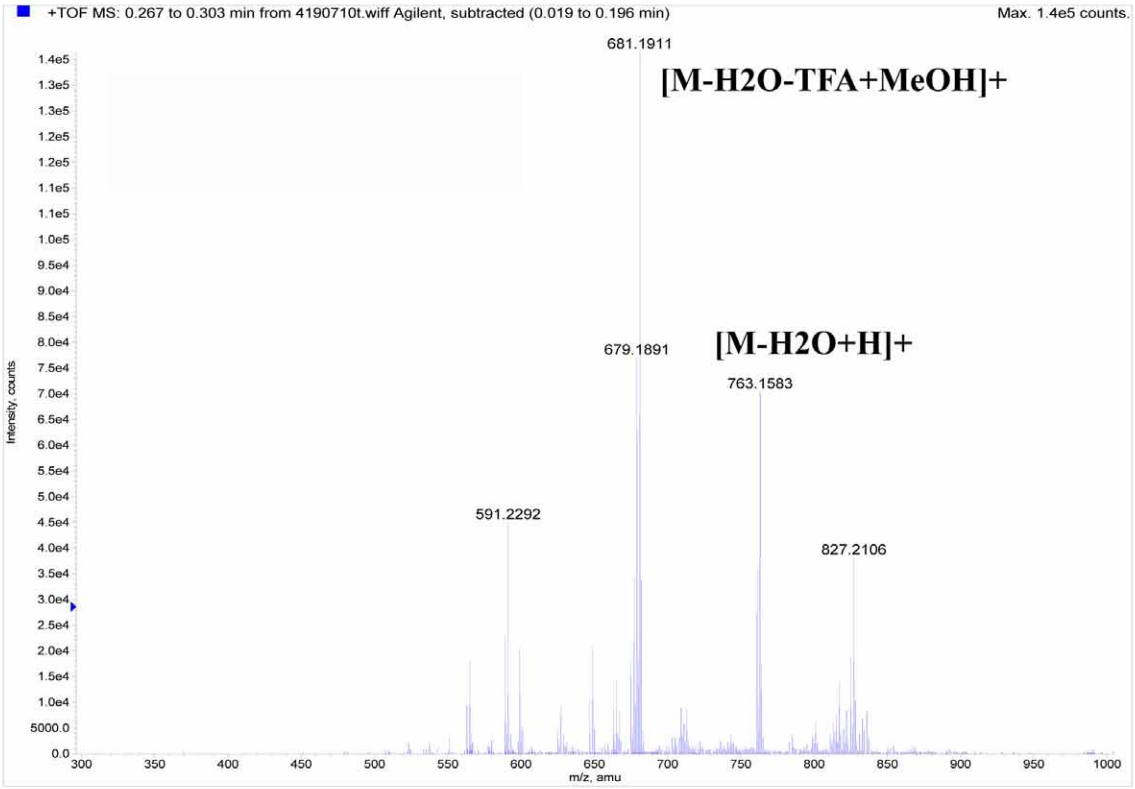


Measured Mass 813.1714

Element	Low Limit	High Limit
C	25	35
F	4	8
H	20	40
N	1	3
O	3	5
Ir	0	1
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C30 H31 N2 O4 F6 Na Ir	813.1715	-0.1	-0.1	14
C33 H30 N2 O3 F5 Na Ir	813.1704	1.0	1.3	18

Figure S28. HRESI-MS of 1-TFA_2.



Measured Mass 763.1583

Element	Low Limit	High Limit
C	23	33
F	5	7
H	20	40
Ir	0	2
N	0	3
O	2	6

Formula	Calculated Mass	mDaError	ppmError	RDB
C28 H28 N2 O4 F6 Ir	763.1583	0.0	0.0	14
C25 H29 N2 O5 F7 Ir	763.1594	-1.1	-1.5	10
C31 H27 N2 O3 F5 Ir	763.1571	1.2	1.5	18
C28 H27 N3 O2 F7 Ir	763.1621	-3.8	-5.0	14.5

Figure S29. HRESI-MS of 1-$TFA_2(H_2O)$.

X-ray structure determination of 1-TFA$_2$. Suitable yellow crystals of **1-TFA$_2$** were grown by vapor diffusion of pentane into a CH_2Cl_2 solution. Diffraction data on a single crystal of cubic shape (0.1 x 0.05 x 0.05 mm^3) were collected at 110 K. A hemisphere of data was collected up to a resolution of 0.82 Å. All non-hydrogen atoms were located in the difference-Fourier maps and refined by least squares using SHELX with 4,036 independent reflections within the range of θ: 1.8^0 to 25.7^0 (completeness 67.4%). Absorption corrections were applied by SADABS [2], with an $R_{(int)}$ = 2.2 %. Calculated hydrogen position were input and refined in a riding manner along with the corresponding carbons. The thermal ellipsoid plot is shown in Figure S30. Crystal data and refinement parameters can be found in Table 15. Selected bond lengths and angles can be found in Table 17.

Final structure refinement for $C_{31}H_{31}N_2O_5F_6Ir$ resulted in a R_1 = 5.2 % and $_wR_2$ = 12.9 %. The data to parameter ratio is 10 : 1. The crystal system found is triclinic, space group P1, with Z equal to 2 and unit cell dimensions: a = 11.83 Å b = 12.88 Å, c = 13.06 Å, α = 60.84^o, β = 70.91^o and γ = 67.39^o. There is one molecule in the asymmetric unit.

Initially, we attempted to solve the structure in the more common triclinic space group P-1. When our P-1 attempts yielded no chemically plausible results we continued the refinement in P1. After a few cycles of least-squares refinement the structure was found to be twinned. In order to refine the structure correctly we noticed the two molecule's reciprocal lattices coincided exactly (pseudo-merohedry) with one other. The procedure was relatively simple to fix. The command "TWIN" was applied the instruction file (*.ins deck) and used to transform the hkl indices of one component into the other. We made one more attempt to phase the TWIN refined P1 molecule into the P-1 space group. The well behaved P1 structure fell apart instantly even with large (10,000) dampening factors.

There is one methanol molecule located in the crystal lattice. The methanol did refine well and were therefore included in the final anisotropic results.

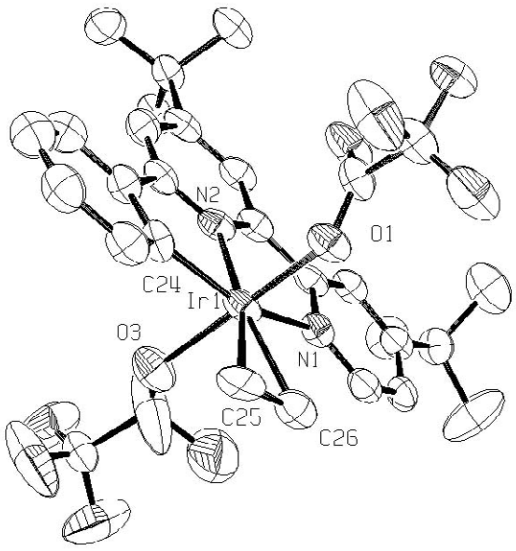


Figure S30. Thermal ellipsoid plot of **Ir(NN^{tBu}C)TFA$_2$(C$_2$H$_4$)** with 50% probability. Hydrogen's and methanol were removed for clarity.

Reaction of 1-TFA in HTFA: Upon dissolving **1-TFA** in neat HTFA ethane is generated to form the Ir(NN^{tBu}C)TFA$_2$(C$_2$H$_4$) complex as the major product and a minor amount of the solvent complex. When the solution is heated at elevated temperatures such as 160 or 180 ^{o}C, ethylene is quickly lost to form a mixture of the solvent (**1A**) and κ^2-trifluoroacetate (**1B**) complex by NMR analysis (Figure S31). Integration of the aromatic region confirmed that the NNC ligand remained cyclometalated to the Ir(III) center. The NMR of this mixture matches the NMR of the aquo complex in DTFA. Both the solvent and κ^2-trifluoroacetate complex could not be separated and isolated. At longer times (15 h) these species disappear and new unidentified peaks form. To further support to formation of bis TFA complex these intermediates were trapped with pyridine. Upon, treating the resulting residue with pyridine and gently heating, the

(NNC)Ir(TFA)$_2$(C_5H_5N)

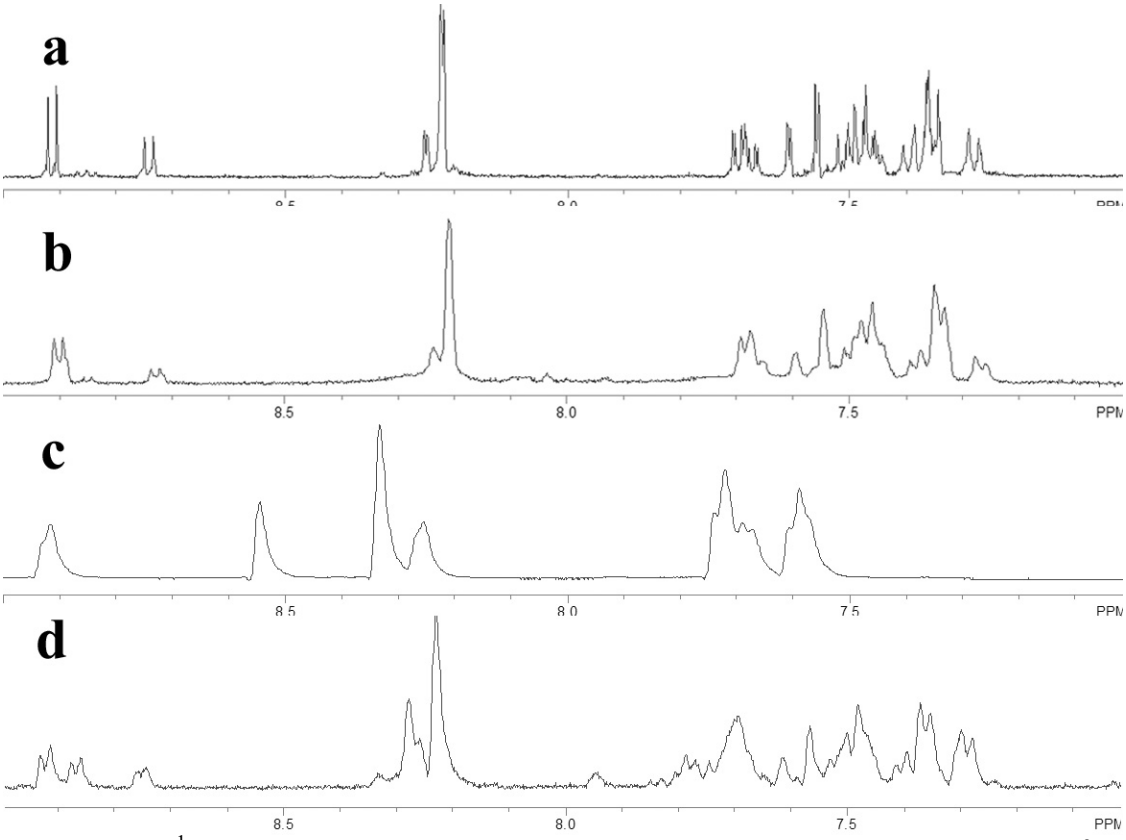


Figure S31. ^{1}H NMR of **1-TFA$_2$** in HTFA, aromatic region. a.) after heating at 180 ^{o}C for 1 h. b). spectra of aquo complex in HTFA. c). spectra of free ligand in HTFA. d). after heating at 160 ^{o}C for 15 h.

complex was isolated after passing through silica gel with CH_2Cl_2. At lower temperatures (140^{o}C) both **1A** and **1B** are more stable (Figure S32).

Data for (NNC^{tBu})Ir(TFA)$_2$(C_5H_5N): HRMALDI-MS (anthracene matrix) calc. for $C_{33}H_{32}N_3O_4F_6Ir$: 841.1921, found 841.1861 M^+, 728.2234 $(M\text{-}TFA)^+$.

^{1}H NMR 9.07(dd, 2H, ^{3}J = 6.6, ^{4}J = 1.6, o-Py), 8.42(d, 1H, ^{3}J = 5.7, H-1), 8.03-8.06(m, 2H, H-4, p-Py), 7.85(d, 1H, ^{4}J = 1.6, H-9), 7.80(d, 1H, ^{4}J = 1.6, H-7), 7.66(dd, 1H, ^{3}J = 7.7, ^{4}J = 1.4, H-15), 7.62(m, 2H, m-Py), 7.55(dd, 1H, ^{3}J = 5.7, ^{4}J = 1.8, H-2), 7.13(dt, 1H, ^{3}J = 7.4, ^{4}J = 1.5, H-

13), 7.04(dt, 1H, ^{3}J = 7.4, ^{4}J = 1.4, H-14), 6.81(dd, 1H, ^{3}J = 7.5, ^{4}J = 1.2, H-12), 1.54(s, 9H, CMe_3), 1.46(s, 9H, CMe_3). ^{13}C NMR 168.37, 163.73, 163.65, 160.02, 157.90, 151.764, 149.45, 148.32, 140.93, 137.70, 133.12, 130.06, 125.80, 124.76, 123.78, 123.40, 119.13, 115.07, 114.49, 35.58, 31.26, 30.74.

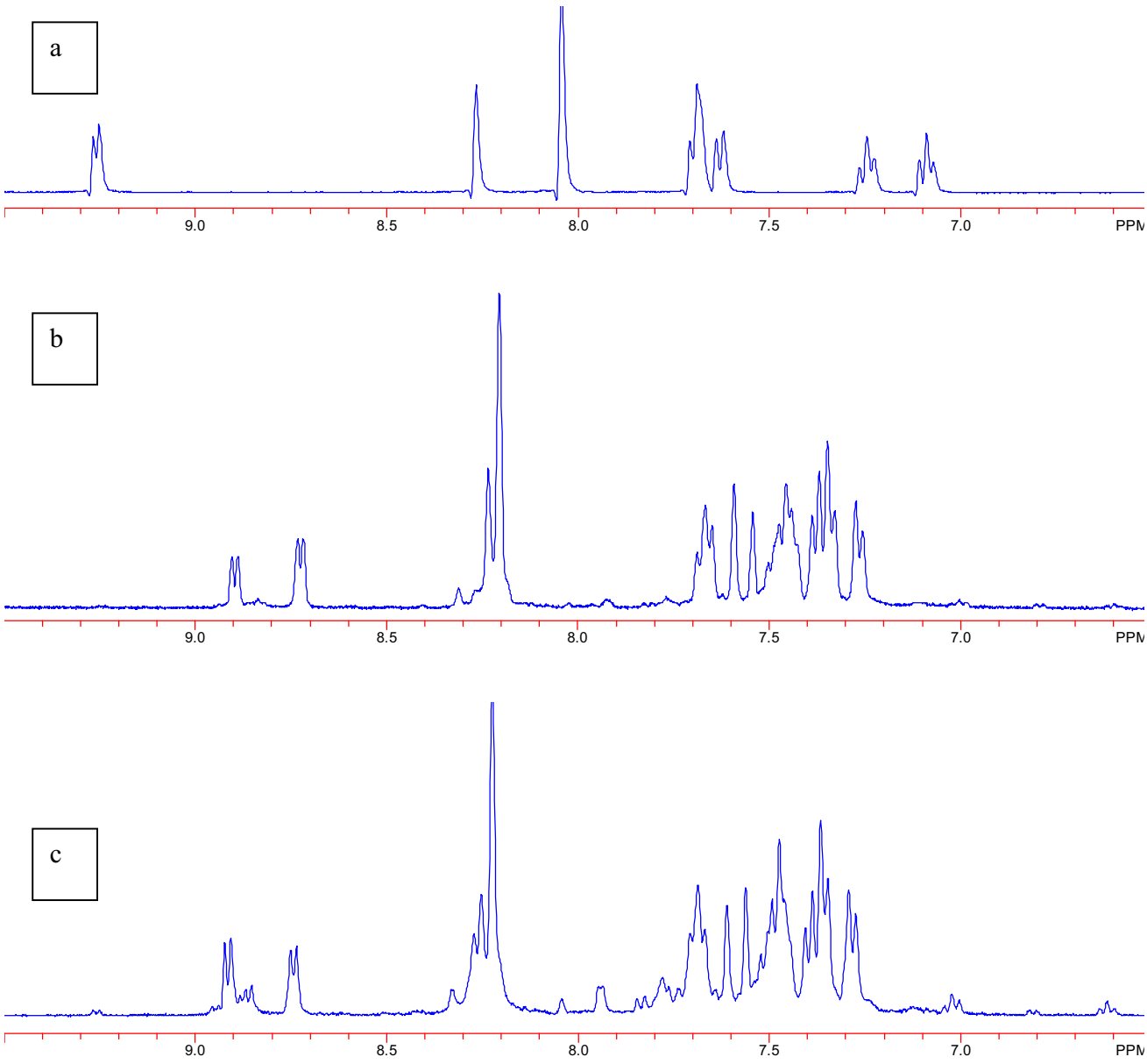
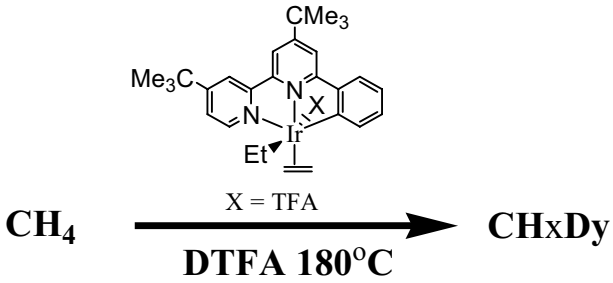


Figure S32. ^{1}H NMR of 1-TFA_2 in HTFA, aromatic region. a.) Before heating. b.) After heating at 140 ^{o}C for 5.5 h. c.) After heating at 140 ^{o}C for 22 h.

Methane H/D exchange studies: Catalytic H-D exchange reactions were quantified by monitoring the increase of deuterium into CH_4 by GC-MS analyses. This was achieved by deconvolution of the mass fragmentation pattern obtained from the MS analysis, using a deconvolution program developed with Microsoft EXCEL. An important assumption used in the program is that there are no isotope effects on the fragmentation pattern of methane due to replacement of H with D. Fortunately, because of the relative stability of the parent ion towards fragmentation, it can be used reliably to quantify the exchange reactions. The mass range from 12 to 21 was examined for each reaction and compared to a control reaction where no metal catalyst was added. The program was calibrated with known mixtures of methane isotopoloques. The results obtained from this method are reliable to within 5%.

Reaction of 1-TFA with methane and acids: In a typical experiment a resealable metal reactor with a glass insert and stir bar was loaded with 10-20 mg of **1-TFA**, and then under argon 1 mL of solvent (trifluoroacetic acid-d_1 or acetic acid-d_4) was added. The reactor was then flushed with 514.7 psi methane (3 times) then pressurized with 514.7 psi methane while stirring. Control reactions were also prepared by identical procedures only without catalyst. The reactors was then placed in a preheated block at 180^{o}C, and heated for 2 to 24h. After the reaction, the reactors were allowed to cool back to ambient temperature, and part of the headspace was transferred to a evacuate 2 mL vial fitted with a septa. The headspace of the catalyst runs and control runs was then analyzed by GC-MS (Table 1). There was no background H/D exchange observed between methane and DTFA. The reactors were then opened and the reaction mixtures were fully homogeneous with no signs of decomposition. In the reaction with acetic acid-d_4 no H/D exchange was observed, however, small amounts of CD_4 are observed, likely resulting from the decarboxylation of DOAc to produce CO_2 and CD_4.

Table 1. H/D exchange between methane and acids[a].



[a] Reaction conditions: CH_4 (514.7 psi, 5 mmol), 1 mL DTFA.

Entry	Time (h)	CH_3D	CH_2D_2	C_HD_3	CD_4	TON
1	2	20.71	6.15	1.15	0.64	145.4
2	2	22.01	7.02	1.50	0.65	160.8
3	3	26.14	17.01	7.76	1.63	172.5
4	3	27.06	10.07	2.22	0.31	159.2
5	19	24.87	10.29	2.54	0.67	164.4
6[b]	6	0	0	0	0	0
7[c]	45	11.11	2.26	0.00	0.21	61.9

[b] Reaction conditions: 160°C, + 0.2 mL DMSO.
[c] Reaction conditions: 105°C.

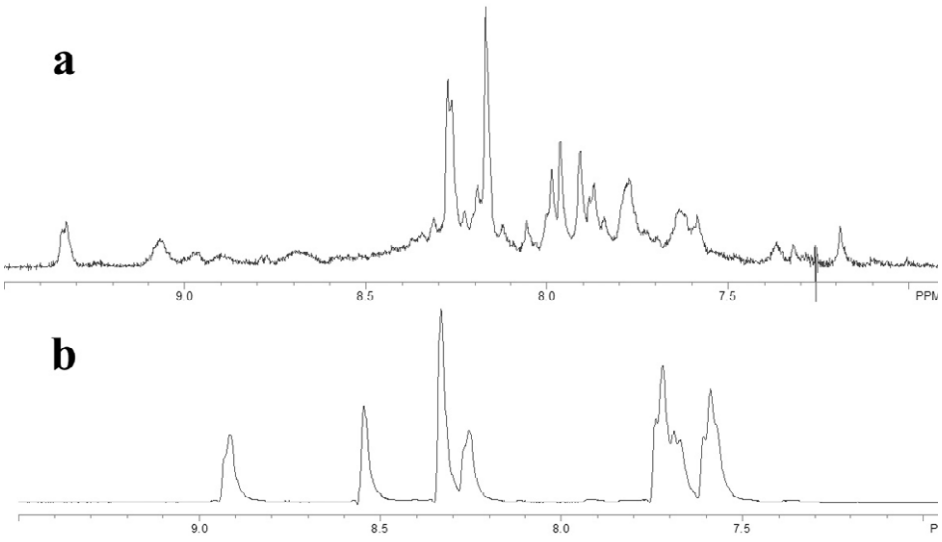


Figure S33. a.) ^{1}H NMR of the aromatic region of the reaction mixture from the H/D exchange reaction between methane and DTFA with **1-TFA**. B.) ^{1}H NMR of the aromatic region of free ligand in DTFA.

Reaction of 1-TFA with methane and acids: Similar rates for H/D exchange were obtained

with a solution of the solvento complex (NNC^{tBu})Ir$(TFA)_2$(HTFA), (Table S2), prepared by preheating **1-TFA** in DTFA in the absence of methane followed by degassing to remove any ethylene, or by using the isolated aquo complex. This shows that the presence of ethylene (1 equiv.) generated by *in-situ* conversion of **1-TFA** to the solvent complex has little impact.

Table S2. Comparision of 1-TFA to the solvent complex.[a]

Entry	Catalyst	CH_3D	CH_2D_2	CHD_3	CD_4	TON	TOF (s^{-1})
1	1-TFA	20.71	6.15	1.15	0.64	145.4	2.02×10^{-2}
2	1-TFA	22.01	7.02	1.50	0.65	160.8	2.23×10^{-2}
3	1-TFA[b]	18.26	6.25	2.81	1.18	148.9	2.07×10^{-2}

[a]. Reaction conditions: 0.3 mol% catalyst, CH_4 (514.7 psi, 5 mmol), 1 mL DTFA, 180°C 2h.
[b]. Solvent complex.

Activation energy for catalytic methane activation: A 14.34 mM stock solution of **1-TFA** in DTFA was prepared, from which 1 mL aliquots were transferred to resealable metal micro reactors with a glass insert and stir bar under argon. The reactor was then flushed with methane then pressurized with 514.7 psi methane while stirring. The reactors were then placed in a preheated block between 105-135 °C. In order to remain under pseudo first order conditions the TOF's were measured at or near 10% conversion. The activation energy for the overall methane activation was obtained by plotting Ln(TOF/T) versus 1/T (Figure S3). Using the Linest function from Excel the error in the slope was determined. The error in delta H was calculated form the error in the slope. error delta H = (((error in slope)*8.314 J/Kmol)/4.184J)/1000

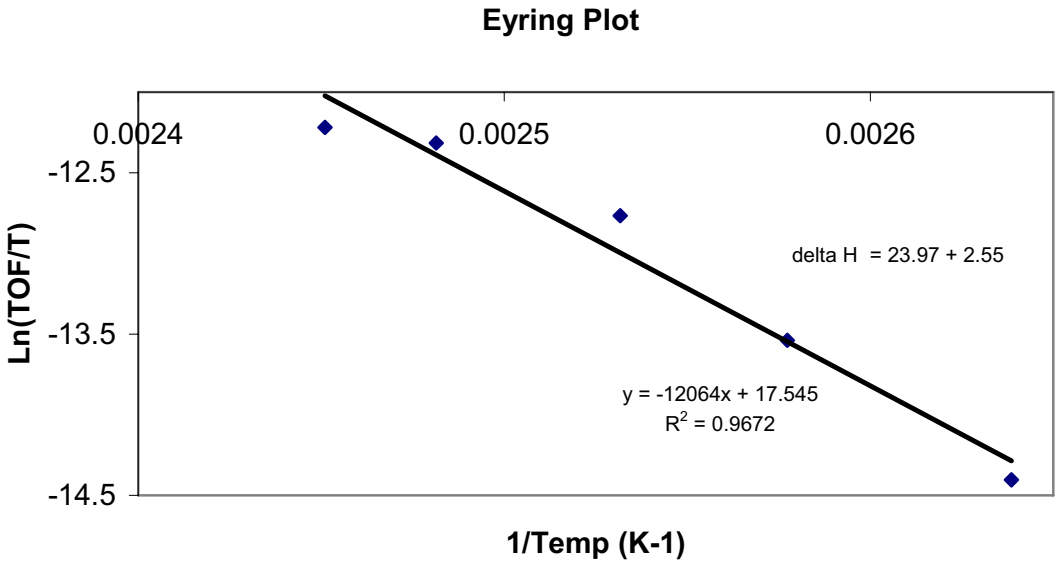
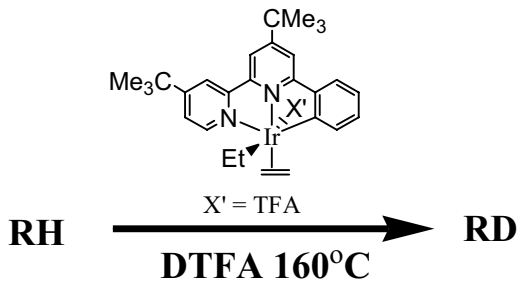


Figure S34. Eyring plot for the catalytic methane activation with **1-TFA**.

Reaction of 1-TFA with alkanes and acids: In a typical experiment a 4 mL Schlenck bomb was loaded 0.2 mL of alkane and 1 mL of ~10 mM stock solution of 1-TFA in DTFA under argon. Control reactions were also prepared by identical procedures only without catalyst. The reactors were then placed in a preheated oil bath block at 160°C, and monitored by GC-MS.

Table 3. H/D exchange between alkanes and DTFA with 1-TFA.



Entry	Alkane	Time (h)	% conversion
1	Octane	6.5	67.98
2	Cyclooctane	6.5	36.86

2	cyclohexane	6.5	97.34

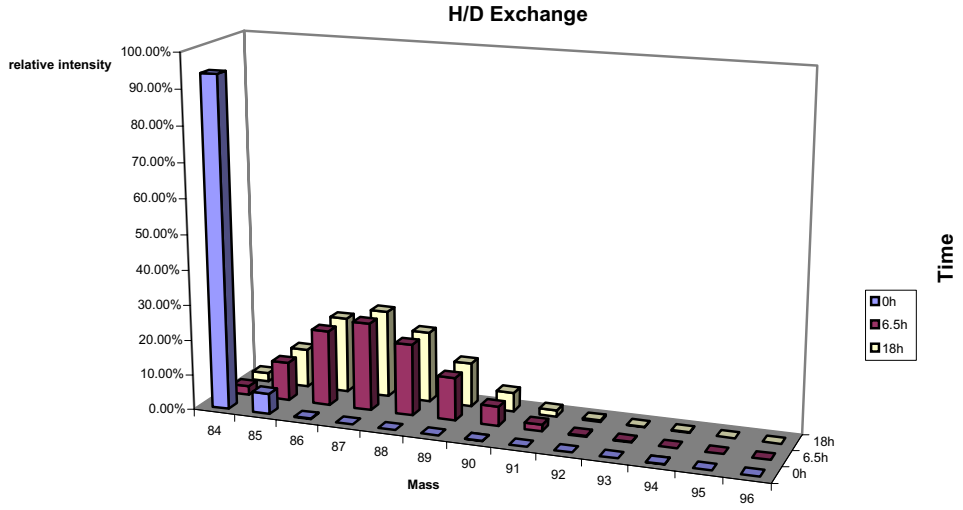


Figure S35. H/D exchange between Cylcohexane/DTFA w/1-TFA

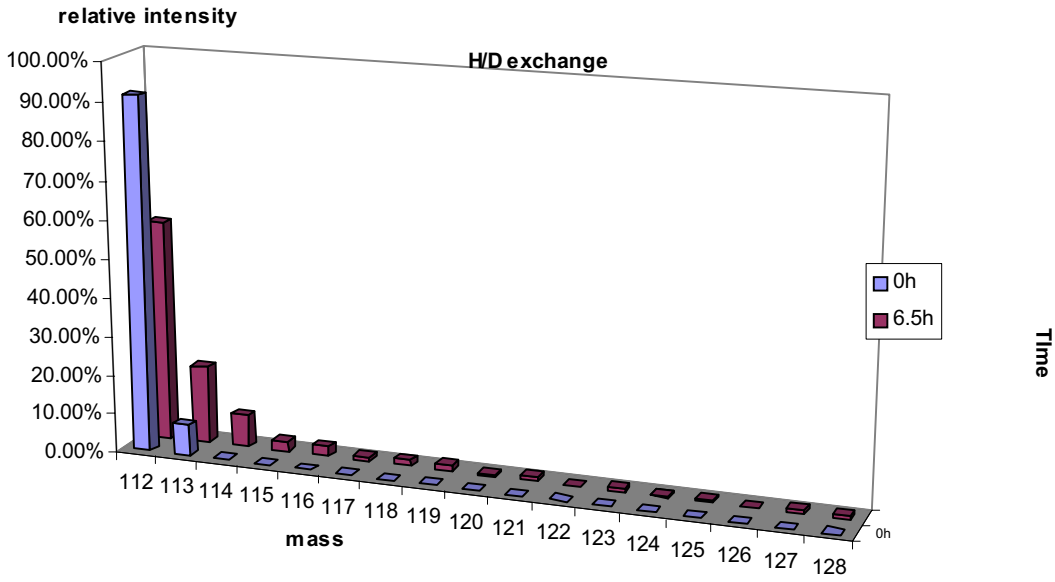


Figure S36. H/D exchange between Cylcooctane/DTFA w/1-TFA

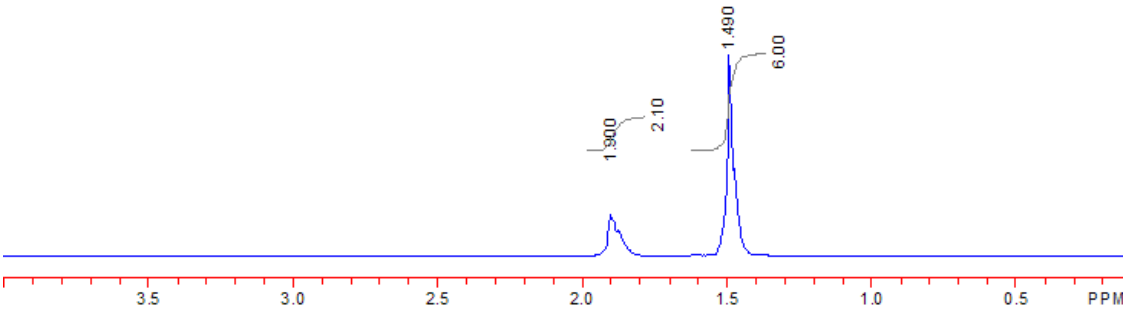


Figure S37. ^{2}H NMR of H/D exchange between octane/DTFA w/1-TFA after 30 min at 160 ^{o}C.

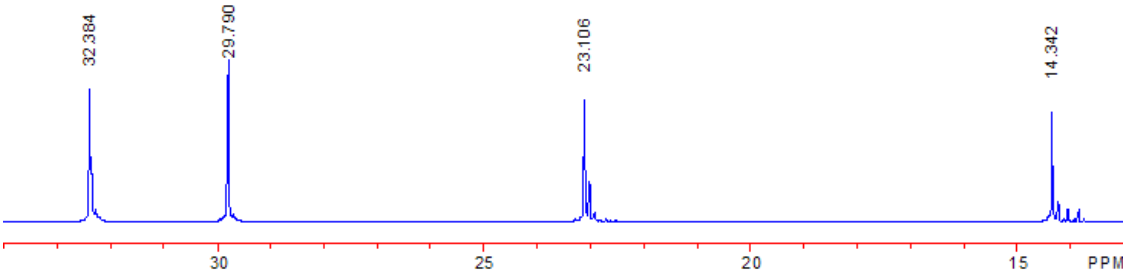
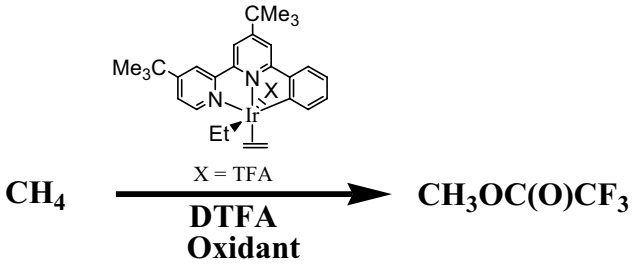


Figure S38. ^{13}C NMR of H/D exchange between octane/DTFA.

Table 4. Oxidation of Methane to Methyltrifluoroacetate[a].



[a] Reaction conditions: CH_4 (514.7 psi, 5 mmol), 1 ml TFA, 180^{o}C

Entry	[Catalyst]	Time (h)	Oxidant (mmol)	MeTFA (mmols)	TON
1[b]	16.66	6	PITFA (0.31)	0.0	
2	0.0	3	$NaIO_4$ (0.42)	0.106	
3	14.87	3	$NaIO_4$ (0.42)	0.0936[c]	6.3
4[b]	0	5	$NaIO_4$ (0.09)	0.023	N/A
5[b]	13.88	5	$NaIO_4$ (0.09)	0.027[c]	2.0
6	0	3	KIO_3	1.56×10^{-2}	
7	14.87	3	KIO_3	2.56×10^{-2c}	1.7

8	27.05	2	N_2O[d]	0.0	
9[b]	17.0	8.5	PyO	0.0	
10[b]	10.85	5	UHP	0.0	
11[b]	0	5	$Na_2S_2O_8$ (0.43)	9.9×10^{-3}	
12	10.85	5	$Na_2S_2O_8$ (0.43)	4.7×10^{-3}[c]	0.4
13[b]	13.16	6	$K_2Os(O)_2(OH)_4$ (0.103)	1.17×10^{-2}	0.9
14[b]	16.66	6	OsO_4 (0.33)	1.47×10^{-2}	0.9

[b] 160°C [c] Corrected values = observed - control. [d] Reaction Conditions: N_2O = 314.7 psi CH_4 = 514.7 psi.

Reaction of 1-TFA with methane and oxidant: A resealable metal reactor with a glass insert and stir bar, was loaded with oxidant $NaIO_4$ (90 mg, 0.4207 mmol) then 10.5 mg of **1-TFA** (0.01487 mmol) in 1 mL of trifluoroacetic acid-d_1 was added under argon. While stirring, the reactor was charged with 514.7 psi of methane. A control reaction was also prepared under identical conditions only without catalyst. The reactors were then heated at 180°C for 3h. The reactors were then opened and 5 μL of acetic acid was then added, there was no visible sign of decomposition. ^{1}H NMR analysis of the solution showed CH_3TFA formation in both reactions (Table 4). CH_3TFA formation was also supported by comparison to authentic sample by ^{13}C NMR, GC-MS, and HPLC.

X-ray Data:

Table 5. Crystal data and structure refinement for **1-Cl**.

Identification code	tj5m	
Empirical formula	C57 H66 Cl4 Ir2 N4	
Formula weight	1333.34	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.9695(11) Å	α= 90°.
	b = 29.356(3) Å	β= 104.947(2)°.
	c = 16.8671(15) Å	γ = 90°.
Volume	6204.6(9) $Å^3$	
Z	4	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	4.493 mm^{-1}	
F(000)	2632	
Crystal size	0.10 x 0.05 x 0.02 mm^3	
Theta range for data collection	1.39 to 27.54°.	
Index ranges	-16<=h<=13, -37<=k<=38, -14<=l<=21	
Reflections collected	36987	
Independent reflections	13971 [R(int) = 0.0597]	
Completeness to theta = 27.54°	97.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13971 / 0 / 619	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.1676	
R indices (all data)	R1 = 0.1051, wR2 = 0.1805	
Extinction coefficient	0.00085(9)	
Largest diff. peak and hole	3.663 and -2.400 $e.Å^{-3}$	

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1-Cl**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	4976(1)	9157(1)	6790(1)	25(1)
Ir(2)	174(1)	1842(1)	4165(1)	28(1)
Cl(1)	4272(2)	8519(1)	5835(2)	40(1)
Cl(2)	74(2)	2442(1)	5181(2)	43(1)
Cl(3)	810(5)	2557(2)	7702(4)	121(2)
Cl(4)	1856(6)	1690(2)	7866(3)	131(3)
N(1)	4175(6)	8939(3)	7584(5)	25(2)
N(2)	6086(6)	8691(3)	7564(5)	24(2)
N(3)	-473(6)	1384(3)	4920(6)	28(2)
N(4)	1494(6)	1593(3)	4964(5)	25(2)
C(1)	3555(8)	9516(3)	6386(7)	27(2)
C(2)	3196(9)	9820(4)	5726(7)	34(3)
C(3)	2187(9)	10009(4)	5572(7)	35(3)
C(4)	1476(9)	9913(4)	6030(7)	36(3)
C(5)	1809(9)	9619(4)	6692(7)	35(3)
C(6)	2844(8)	9423(3)	6879(6)	25(2)
C(7)	3198(8)	9106(3)	7562(6)	26(2)
C(8)	2666(8)	8973(4)	8135(7)	32(2)
C(9)	3105(9)	8675(4)	8752(8)	39(3)
C(10)	4118(9)	8500(4)	8766(8)	37(3)
C(11)	4633(8)	8635(4)	8181(7)	30(2)
C(12)	5720(8)	8493(4)	8170(7)	33(2)
C(13)	6320(8)	8186(3)	8703(6)	27(2)
C(14)	7350(8)	8067(4)	8672(7)	30(2)
C(15)	7706(9)	8276(4)	8058(7)	37(3)
C(16)	7066(8)	8571(4)	7511(7)	31(2)
C(17)	2541(9)	8516(5)	9406(8)	45(3)
C(18)	1513(12)	8795(6)	9335(11)	83(6)
C(19)	2253(10)	8026(5)	9279(10)	61(4)
C(20)	3286(13)	8587(6)	10251(9)	68(4)
C(21)	8008(9)	7724(4)	9288(7)	38(3)
C(22)	7482(11)	7261(4)	9153(9)	52(4)
C(23)	8055(11)	7885(5)	10160(8)	53(3)
C(24)	9142(10)	7678(5)	9175(9)	52(4)
C(25)	6196(8)	9260(4)	6135(7)	36(3)
C(26)	5321(9)	9526(4)	5752(8)	40(3)
C(27)	5650(9)	9695(4)	7587(7)	35(3)
C(28)	5325(12)	9759(5)	8344(9)	59(4)
C(29)	-1496(8)	1294(3)	4898(7)	30(2)
C(30)	-1791(8)	1067(4)	5534(7)	30(2)
C(31)	-1043(8)	923(3)	6209(7)	31(2)
C(32)	24(9)	995(4)	6221(7)	32(2)
C(33)	278(8)	1220(3)	5581(7)	26(2)
C(34)	1390(8)	1318(3)	5574(6)	25(2)
C(35)	2264(8)	1161(3)	6138(7)	29(2)
C(36)	3288(8)	1290(3)	6112(6)	28(2)
C(37)	3354(8)	1580(3)	5467(7)	30(2)
C(38)	2473(8)	1724(3)	4902(7)	27(2)
C(39)	2407(8)	2046(3)	4242(7)	28(2)
C(40)	3334(9)	2228(4)	4074(7)	34(2)
C(41)	3236(10)	2575(4)	3498(7)	40(3)
C(42)	2228(10)	2731(4)	3085(8)	42(3)

C(43)	1320(9)	2530(4)	3226(7)	37(3)
C(44)	1350(8)	2184(3)	3798(7)	28(2)
C(45)	-1363(9)	715(4)	6946(8)	40(3)
C(46)	-2199(12)	325(5)	6642(10)	62(4)
C(47)	-1881(12)	1086(5)	7343(9)	55(4)
C(48)	-389(11)	535(6)	7611(9)	75(5)
C(49)	4310(8)	1139(4)	6759(7)	33(2)
C(50)	4048(9)	803(4)	7365(8)	42(3)
C(51)	4859(11)	1570(4)	7190(8)	52(4)
C(52)	5040(9)	888(4)	6312(8)	41(3)
C(53)	-1507(10)	1984(4)	3576(8)	46(3)
C(54)	-839(9)	2258(5)	3215(8)	50(3)
C(55)	206(10)	1334(4)	3301(7)	42(3)
C(56)	762(9)	933(5)	3551(9)	53(4)
C(57)	1440(20)	2165(6)	7246(11)	103(7)

Table 7. Bond lengths [Å] and angles [°] for **1-Cl**.

Ir(1)-N(1)	2.001(8)	C(33)-C(34)	1.474(13)
Ir(1)-C(1)	2.078(10)	C(34)-C(35)	1.359(14)
Ir(1)-C(27)	2.110(12)	C(35)-C(36)	1.393(14)
Ir(1)-N(2)	2.165(8)	C(36)-C(37)	1.401(15)
Ir(1)-C(25)	2.172(10)	C(36)-C(49)	1.548(14)
Ir(1)-C(26)	2.200(11)	C(37)-C(38)	1.354(14)
Ir(1)-Cl(1)	2.488(3)	C(38)-C(39)	1.445(14)
Ir(2)-N(4)	2.024(8)	C(39)-C(40)	1.410(14)
Ir(2)-C(44)	2.052(10)	C(39)-C(44)	1.440(15)
Ir(2)-C(55)	2.092(12)	C(40)-C(41)	1.390(16)
Ir(2)-N(3)	2.163(8)	C(41)-C(42)	1.391(17)
Ir(2)-C(54)	2.167(11)	C(42)-C(43)	1.392(15)
Ir(2)-C(53)	2.190(12)	C(43)-C(44)	1.394(15)
Ir(2)-Cl(2)	2.485(3)	C(45)-C(47)	1.522(17)
Cl(3)-C(57)	1.704(18)	C(45)-C(48)	1.550(18)
Cl(4)-C(57)	1.745(17)	C(45)-C(46)	1.570(17)
N(1)-C(7)	1.350(12)	C(49)-C(50)	1.521(16)
N(1)-C(11)	1.362(13)	C(49)-C(51)	1.540(15)
N(2)-C(16)	1.344(13)	C(49)-C(52)	1.541(16)
N(2)-C(12)	1.362(14)	C(53)-C(54)	1.428(18)
N(3)-C(29)	1.343(12)	C(55)-C(56)	1.389(18)
N(3)-C(33)	1.365(13)		
N(4)-C(34)	1.340(13)	N(1)-Ir(1)-C(1)	79.2(4)
N(4)-C(38)	1.356(12)	N(1)-Ir(1)-C(27)	90.8(4)
C(1)-C(2)	1.410(15)	C(1)-Ir(1)-C(27)	91.0(4)
C(1)-C(6)	1.418(14)	N(1)-Ir(1)-N(2)	76.8(3)
C(2)-C(3)	1.383(15)	C(1)-Ir(1)-N(2)	156.0(4)
C(3)-C(4)	1.375(16)	C(27)-Ir(1)-N(2)	89.3(4)
C(4)-C(5)	1.390(15)	N(1)-Ir(1)-C(25)	163.1(4)
C(5)-C(6)	1.418(14)	C(1)-Ir(1)-C(25)	117.7(4)
C(6)-C(7)	1.461(14)	C(27)-Ir(1)-C(25)	89.1(4)
C(7)-C(8)	1.380(14)	N(2)-Ir(1)-C(25)	86.3(4)
C(8)-C(9)	1.367(15)	N(1)-Ir(1)-C(26)	159.7(4)
C(9)-C(10)	1.405(15)	C(1)-Ir(1)-C(26)	80.5(4)
C(9)-C(17)	1.546(16)	C(27)-Ir(1)-C(26)	90.2(5)
C(10)-C(11)	1.386(15)	N(2)-Ir(1)-C(26)	123.4(4)
C(11)-C(12)	1.474(15)	C(25)-Ir(1)-C(26)	37.1(4)
C(12)-C(13)	1.366(15)	N(1)-Ir(1)-Cl(1)	91.4(3)
C(13)-C(14)	1.395(14)	C(1)-Ir(1)-Cl(1)	91.4(3)
C(14)-C(15)	1.383(16)	C(27)-Ir(1)-Cl(1)	177.0(3)
C(14)-C(21)	1.537(15)	N(2)-Ir(1)-Cl(1)	89.4(2)
C(15)-C(16)	1.376(15)	C(25)-Ir(1)-Cl(1)	88.2(3)
C(17)-C(19)	1.49(2)	C(26)-Ir(1)-Cl(1)	88.4(4)
C(17)-C(20)	1.52(2)	N(4)-Ir(2)-C(44)	79.1(4)
C(17)-C(18)	1.543(17)	N(4)-Ir(2)-C(55)	92.4(4)
C(21)-C(22)	1.510(18)	C(44)-Ir(2)-C(55)	89.4(4)
C(21)-C(23)	1.531(18)	N(4)-Ir(2)-N(3)	76.9(3)
C(21)-C(24)	1.537(16)	C(44)-Ir(2)-N(3)	156.0(4)
C(25)-C(26)	1.393(15)	C(55)-Ir(2)-N(3)	92.8(4)
C(27)-C(28)	1.457(18)	N(4)-Ir(2)-C(54)	160.7(4)
C(29)-C(30)	1.399(15)	C(44)-Ir(2)-C(54)	81.8(5)
C(30)-C(31)	1.359(15)	C(55)-Ir(2)-C(54)	90.2(5)
C(31)-C(32)	1.395(14)	N(3)-Ir(2)-C(54)	122.1(4)
C(31)-C(45)	1.535(16)	N(4)-Ir(2)-C(53)	160.6(4)
C(32)-C(33)	1.377(15)	C(44)-Ir(2)-C(53)	120.1(4)

C(55)-Ir(2)-C(53)	90.9(5)	C(18)-C(17)-C(9)	110.1(11)
N(3)-Ir(2)-C(53)	83.9(4)	C(22)-C(21)-C(23)	109.1(10)
C(54)-Ir(2)-C(53)	38.3(5)	C(22)-C(21)-C(24)	108.2(11)
N(4)-Ir(2)-Cl(2)	89.0(2)	C(23)-C(21)-C(24)	110.1(11)
C(44)-Ir(2)-Cl(2)	92.0(3)	C(22)-C(21)-C(14)	109.7(10)
C(55)-Ir(2)-Cl(2)	178.2(3)	C(23)-C(21)-C(14)	109.0(10)
N(3)-Ir(2)-Cl(2)	86.4(2)	C(24)-C(21)-C(14)	110.8(9)
C(54)-Ir(2)-Cl(2)	88.9(4)	C(26)-C(25)-Ir(1)	72.5(6)
C(53)-Ir(2)-Cl(2)	87.4(4)	C(25)-C(26)-Ir(1)	70.3(6)
C(7)-N(1)-C(11)	119.1(9)	C(28)-C(27)-Ir(1)	119.3(8)
C(7)-N(1)-Ir(1)	120.7(7)	N(3)-C(29)-C(30)	122.5(10)
C(11)-N(1)-Ir(1)	120.1(7)	C(31)-C(30)-C(29)	120.8(10)
C(16)-N(2)-C(12)	117.2(9)	C(30)-C(31)-C(32)	117.2(10)
C(16)-N(2)-Ir(1)	128.2(7)	C(30)-C(31)-C(45)	121.2(9)
C(12)-N(2)-Ir(1)	114.6(7)	C(32)-C(31)-C(45)	121.5(10)
C(29)-N(3)-C(33)	116.4(9)	C(33)-C(32)-C(31)	119.9(10)
C(29)-N(3)-Ir(2)	129.5(7)	N(3)-C(33)-C(32)	123.0(9)
C(33)-N(3)-Ir(2)	113.3(6)	N(3)-C(33)-C(34)	114.7(9)
C(34)-N(4)-C(38)	120.8(9)	C(32)-C(33)-C(34)	122.2(10)
C(34)-N(4)-Ir(2)	119.5(7)	N(4)-C(34)-C(35)	120.7(9)
C(38)-N(4)-Ir(2)	119.6(7)	N(4)-C(34)-C(33)	114.6(9)
C(2)-C(1)-C(6)	116.9(9)	C(35)-C(34)-C(33)	124.6(9)
C(2)-C(1)-Ir(1)	131.6(8)	C(34)-C(35)-C(36)	121.0(10)
C(6)-C(1)-Ir(1)	111.5(7)	C(35)-C(36)-C(37)	116.1(10)
C(3)-C(2)-C(1)	120.4(11)	C(35)-C(36)-C(49)	123.3(10)
C(4)-C(3)-C(2)	123.5(11)	C(37)-C(36)-C(49)	120.5(9)
C(3)-C(4)-C(5)	117.6(10)	C(38)-C(37)-C(36)	121.8(10)
C(4)-C(5)-C(6)	120.7(11)	C(37)-C(38)-N(4)	119.6(10)
C(1)-C(6)-C(5)	120.8(10)	C(37)-C(38)-C(39)	128.2(10)
C(1)-C(6)-C(7)	117.7(9)	N(4)-C(38)-C(39)	112.0(9)
C(5)-C(6)-C(7)	121.4(10)	C(40)-C(39)-C(44)	122.4(10)
N(1)-C(7)-C(8)	120.8(9)	C(40)-C(39)-C(38)	121.2(10)
N(1)-C(7)-C(6)	110.8(9)	C(44)-C(39)-C(38)	116.4(9)
C(8)-C(7)-C(6)	128.3(9)	C(41)-C(40)-C(39)	119.2(11)
C(9)-C(8)-C(7)	121.9(10)	C(40)-C(41)-C(42)	119.8(11)
C(8)-C(9)-C(10)	116.9(10)	C(41)-C(42)-C(43)	120.1(11)
C(8)-C(9)-C(17)	123.8(10)	C(42)-C(43)-C(44)	123.6(11)
C(10)-C(9)-C(17)	119.3(10)	C(43)-C(44)-C(39)	114.7(9)
C(11)-C(10)-C(9)	120.2(10)	C(43)-C(44)-Ir(2)	132.5(8)
N(1)-C(11)-C(10)	121.0(10)	C(39)-C(44)-Ir(2)	112.8(7)
N(1)-C(11)-C(12)	114.3(9)	C(47)-C(45)-C(31)	108.3(10)
C(10)-C(11)-C(12)	124.6(10)	C(47)-C(45)-C(48)	107.2(12)
N(2)-C(12)-C(13)	121.7(10)	C(31)-C(45)-C(48)	112.4(10)
N(2)-C(12)-C(11)	114.1(10)	C(47)-C(45)-C(46)	108.7(10)
C(13)-C(12)-C(11)	124.2(10)	C(31)-C(45)-C(46)	109.5(11)
C(12)-C(13)-C(14)	122.0(10)	C(48)-C(45)-C(46)	110.6(12)
C(15)-C(14)-C(13)	115.1(10)	C(50)-C(49)-C(51)	111.8(10)
C(15)-C(14)-C(21)	124.3(9)	C(50)-C(49)-C(52)	106.9(9)
C(13)-C(14)-C(21)	120.6(10)	C(51)-C(49)-C(52)	110.9(10)
C(16)-C(15)-C(14)	121.4(10)	C(50)-C(49)-C(36)	111.1(9)
N(2)-C(16)-C(15)	122.5(10)	C(51)-C(49)-C(36)	107.8(9)
C(19)-C(17)-C(20)	110.1(12)	C(52)-C(49)-C(36)	108.4(9)
C(19)-C(17)-C(18)	108.8(12)	C(54)-C(53)-Ir(2)	70.0(6)
C(20)-C(17)-C(18)	109.2(13)	C(53)-C(54)-Ir(2)	71.7(7)
C(19)-C(17)-C(9)	109.7(11)	C(56)-C(55)-Ir(2)	119.7(9)
C(20)-C(17)-C(9)	109.0(11)	Cl(3)-C(57)-Cl(4)	112.3(10)

Symmetry transformations used to generate equivalent atoms:

Table 8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-Cl**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	22(1)	22(1)	34(1)	4(1)	11(1)	1(1)
Ir(2)	21(1)	26(1)	36(1)	4(1)	7(1)	-1(1)
Cl(1)	29(1)	36(2)	51(2)	-8(1)	5(1)	4(1)
Cl(2)	37(2)	39(2)	58(2)	-7(1)	21(1)	2(1)
Cl(3)	132(5)	131(5)	113(4)	51(4)	53(4)	67(4)
Cl(4)	219(8)	96(4)	72(3)	-10(3)	25(4)	69(4)
N(1)	14(4)	21(4)	40(5)	5(4)	7(4)	2(3)
N(2)	24(4)	22(4)	28(5)	9(3)	9(4)	-3(3)
N(3)	20(4)	23(4)	43(5)	1(4)	12(4)	-5(3)
N(4)	20(4)	23(4)	33(5)	-3(4)	11(4)	-1(3)
C(1)	24(5)	23(5)	36(6)	-4(4)	9(4)	0(4)
C(2)	30(6)	32(6)	36(6)	5(5)	3(5)	-4(5)
C(3)	38(6)	22(5)	38(7)	0(5)	1(5)	8(5)
C(4)	30(6)	27(6)	46(7)	2(5)	4(5)	11(5)
C(5)	25(6)	31(6)	47(7)	2(5)	8(5)	-4(5)
C(6)	25(5)	17(5)	34(6)	-2(4)	6(4)	1(4)
C(7)	25(5)	21(5)	35(6)	1(4)	14(4)	1(4)
C(8)	24(5)	32(6)	44(7)	6(5)	15(5)	3(4)
C(9)	34(6)	45(7)	47(7)	7(6)	26(6)	0(5)
C(10)	38(6)	25(5)	52(7)	16(5)	21(6)	9(5)
C(11)	28(5)	27(5)	36(6)	8(4)	8(5)	1(4)
C(12)	26(5)	29(6)	48(7)	-3(5)	14(5)	-2(4)
C(13)	31(6)	22(5)	31(6)	8(4)	12(5)	1(4)
C(14)	21(5)	30(6)	38(6)	2(5)	5(5)	5(4)
C(15)	27(6)	34(6)	53(8)	6(5)	18(5)	7(5)
C(16)	23(5)	34(6)	39(6)	6(5)	11(5)	4(4)
C(17)	30(6)	57(8)	55(8)	12(6)	23(6)	13(6)
C(18)	59(10)	104(14)	106(14)	58(11)	59(10)	36(9)
C(19)	33(7)	78(11)	82(11)	30(8)	33(7)	6(7)
C(20)	68(10)	81(11)	59(10)	14(8)	26(8)	11(9)
C(21)	28(6)	48(7)	40(7)	10(5)	14(5)	1(5)
C(22)	54(8)	41(7)	64(9)	28(7)	22(7)	17(6)
C(23)	46(8)	53(8)	58(9)	12(7)	12(7)	8(6)
C(24)	33(7)	58(8)	67(9)	26(7)	12(6)	24(6)
C(25)	19(5)	48(7)	49(7)	4(5)	25(5)	0(5)
C(26)	36(6)	42(7)	53(8)	24(6)	31(6)	14(5)
C(27)	32(6)	30(6)	49(7)	15(5)	21(5)	-1(5)
C(28)	62(9)	44(8)	66(10)	-7(7)	10(8)	-11(7)
C(29)	23(5)	28(5)	40(7)	-6(5)	9(5)	-1(4)
C(30)	19(5)	29(6)	45(7)	4(5)	11(5)	-1(4)
C(31)	28(6)	25(5)	45(7)	-2(5)	19(5)	-4(4)
C(32)	28(6)	31(6)	38(6)	0(5)	10(5)	-4(4)
C(33)	24(5)	14(4)	40(6)	1(4)	8(5)	-3(4)
C(34)	23(5)	22(5)	34(6)	2(4)	14(4)	-3(4)
C(35)	25(5)	25(5)	42(7)	-1(5)	17(5)	-1(4)
C(36)	27(5)	23(5)	31(6)	-4(4)	5(4)	0(4)
C(37)	20(5)	28(6)	41(7)	-5(5)	4(5)	-5(4)
C(38)	20(5)	21(5)	40(6)	1(4)	11(4)	3(4)
C(39)	33(6)	14(5)	40(6)	-4(4)	15(5)	0(4)
C(40)	31(6)	33(6)	40(7)	-3(5)	12(5)	-3(5)
C(41)	37(7)	42(7)	46(7)	1(6)	20(6)	-7(5)
C(42)	41(7)	45(7)	45(7)	15(6)	18(6)	-1(6)
C(43)	28(6)	38(6)	48(7)	9(5)	14(5)	3(5)
C(44)	30(6)	22(5)	36(6)	5(4)	15(5)	3(4)
C(45)	27(6)	36(6)	62(9)	3(6)	20(6)	2(5)
C(46)	69(10)	48(8)	81(11)	4(7)	43(9)	-22(7)
C(47)	60(9)	55(9)	59(9)	-8(7)	32(7)	3(7)

C(48)	44(8)	117(14)	62(10)	52(10)	13(7)	0(9)
C(49)	25(5)	34(6)	35(6)	1(5)	0(5)	-3(5)
C(50)	34(6)	44(7)	44(7)	12(6)	3(5)	-1(5)
C(51)	57(9)	43(7)	50(8)	-12(6)	0(7)	-13(6)
C(52)	24(6)	43(7)	58(8)	11(6)	12(5)	10(5)
C(53)	30(6)	46(7)	57(8)	20(6)	0(6)	3(5)
C(54)	25(6)	68(9)	45(8)	21(7)	-10(5)	6(6)
C(55)	45(7)	40(7)	40(7)	0(5)	10(6)	-23(6)
C(56)	19(6)	73(10)	67(9)	-44(8)	13(6)	-7(6)
C(57)	180(20)	77(13)	62(11)	17(10)	50(13)	49(14)

Table 9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1-Cl**.

	x	y	z	U(eq)
H(2)	3650	9896	5384	41
H(3)	1973	10215	5126	41
H(4)	782	10044	5898	43
H(5)	1339	9548	7023	42
H(8)	1975	9093	8099	39
H(10)	4450	8288	9179	44
H(13)	6027	8050	9108	32
H(15)	8408	8215	8012	44
H(16)	7327	8694	7080	38
H(18A)	1111	8665	9699	124
H(18B)	1074	8786	8767	124
H(18C)	1701	9112	9494	124
H(19A)	1859	7931	9675	91
H(19B)	2904	7843	9359	91
H(19C)	1805	7981	8721	91
H(20A)	3908	8387	10318	101
H(20B)	2911	8514	10670	101
H(20C)	3522	8905	10310	101
H(22A)	6753	7284	9214	78
H(22B)	7890	7046	9559	78
H(22C)	7463	7154	8600	78
H(23A)	8460	7664	10557	79
H(23B)	7329	7910	10228	79
H(23C)	8407	8183	10255	79
H(24A)	9102	7578	8614	79
H(24B)	9542	7453	9565	79
H(24C)	9504	7973	9274	79
H(27A)	6434	9653	7738	43
H(27B)	5498	9982	7270	43
H(28A)	5494	9485	8683	88
H(28B)	4555	9816	8213	88
H(28C)	5707	10020	8645	88
H(29)	-2038	1388	4433	36
H(30)	-2525	1012	5494	36
H(32)	575	889	6671	38
H(35)	2175	960	6557	35
H(37)	4036	1677	5424	36
H(40)	4018	2114	4350	41
H(41)	3855	2704	3387	48
H(42)	2160	2976	2707	51
H(43)	642	2635	2916	45
H(46A)	-1832	52	6522	93
H(46B)	-2726	424	6144	93
H(46C)	-2561	255	7071	93
H(47A)	-2472	1223	6929	82
H(47B)	-1351	1321	7573	82
H(47C)	-2153	953	7782	82
H(48A)	65	353	7349	112
H(48B)	-637	345	8002	112
H(48C)	21	793	7901	112
H(50A)	3726	529	7072	63
H(50B)	3544	944	7637	63
H(50C)	4704	721	7777	63
H(51A)	5486	1483	7626	79
H(51B)	4359	1739	7428	79
H(51C)	5082	1763	6790	79
H(52A)	4655	628	6009	62

H(52B)	5678	779	6716	62
H(52C)	5250	1097	5929	62
H(55A)	-543	1250	3035	50
H(55B)	503	1472	2872	50
H(56A)	440	772	3936	79
H(56B)	1508	1004	3821	79
H(56C)	731	739	3072	79
H(57A)	2065	2309	7116	123
H(57B)	946	2066	6723	123

Table 10. Crystal data and structure refinement for **1-TFA**.

Identification code	irnncm_1-tfa_697907	
Empirical formula	C33 H30 F3 Ir N2 O2	
Formula weight	735.79	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.9643(16) Å	α= 90°.
	b = 13.8063(11) Å	β= 91.1910(10)°.
	c = 21.8966(18) Å	γ = 90°.
Volume	6034.1(8) $Å^3$	
Z	8	
Density (calculated)	1.620 Mg/m^3	
Absorption coefficient	4.475 mm^{-1}	
F(000)	2896	
Crystal size	0.13 x 0.03 x 0.01 mm^3	
Theta range for data collection	1.79 to 27.50°.	
Index ranges	-25<=h<=25, -17<=k<=15, -24<=l<=28	
Reflections collected	17914	
Independent reflections	6816 [R(int) = 0.0526]	
Completeness to theta = 27.50°	98.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8773 and 0.5935	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6816 / 16 / 389	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1070	
R indices (all data)	R1 = 0.0806, wR2 = 0.1167	
Largest diff. peak and hole	1.374 and -1.220 $e.Å^{-3}$	

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1-TFA**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	1927(1)	1283(1)	2956(1)	28(1)
F(1)	4251(3)	1305(6)	2465(4)	109(3)
F(2)	4036(3)	1642(5)	1550(3)	83(2)
F(3)	4220(3)	2785(5)	2171(4)	106(3)
N(1)	1741(3)	339(4)	2181(3)	27(1)
N(2)	1487(3)	2169(4)	2333(3)	27(1)
O(1)	2972(3)	1473(4)	2664(3)	50(2)
O(2)	2860(3)	2581(5)	1943(3)	71(2)
C(1)	1825(3)	-619(5)	2142(3)	31(2)
C(2)	1562(4)	-1172(5)	1676(3)	34(2)
C(3)	1181(4)	-761(5)	1205(3)	32(2)
C(4)	1130(3)	247(5)	1229(3)	29(2)
C(5)	1401(3)	771(5)	1709(3)	30(2)
C(6)	1305(3)	1821(5)	1774(3)	28(2)
C(7)	1025(4)	2422(6)	1339(3)	37(2)
C(8)	913(4)	3401(5)	1466(3)	34(2)
C(9)	1107(4)	3722(6)	2043(3)	36(2)
C(10)	1398(3)	3114(5)	2471(3)	30(2)
C(11)	1627(4)	3341(5)	3089(3)	32(2)
C(12)	1585(4)	4284(6)	3325(4)	40(2)
C(13)	1777(4)	4469(6)	3922(4)	44(2)
C(14)	2011(4)	3725(7)	4281(4)	45(2)
C(15)	2064(4)	2795(6)	4049(4)	44(2)
C(16)	1890(4)	2576(5)	3440(3)	32(2)
C(17)	816(4)	-1342(5)	708(3)	38(2)
C(18)	953(7)	-2412(6)	769(5)	86(4)
C(19)	1059(5)	-1017(7)	99(4)	59(3)
C(20)	67(5)	-1176(8)	753(5)	71(3)
C(21)	607(4)	4063(6)	974(4)	42(2)
C(22)	1109(6)	4182(8)	480(5)	75(3)
C(23)	-32(5)	3595(7)	706(5)	68(3)
C(24)	401(7)	5045(7)	1234(5)	86(4)
C(25)	3164(5)	1970(6)	2260(4)	50(2)
C(26)	3909(5)	1966(7)	2103(5)	59(3)
C(27)	2359(5)	0(6)	3376(4)	49(2)
C(28)	2411(5)	778(6)	3793(4)	51(2)
C(29)	997(6)	904(9)	3296(5)	89(6)
C(30)	569(9)	299(14)	2970(8)	51(6)
C(30A)	482(8)	1546(12)	3366(10)	60(6)
C(31)	2824(4)	6641(5)	4956(4)	48(2)
C(32)	2474(6)	6991(7)	4477(4)	162(10)
C(33)	2169(6)	7869(7)	4514(4)	103(5)

Table 12. Bond lengths [Å] and angles [°] for **1-TFA**.

Ir(1)-N(2)	2.019(6)	C(8)-C(9)	1.387(10)
Ir(1)-C(16)	2.078(7)	C(8)-C(21)	1.530(11)
Ir(1)-C(29)	2.081(10)	C(9)-C(10)	1.377(10)
Ir(1)-N(1)	2.166(6)	C(10)-C(11)	1.455(10)
Ir(1)-C(27)	2.168(8)	C(11)-C(16)	1.401(10)
Ir(1)-C(28)	2.170(8)	C(11)-C(12)	1.404(10)
Ir(1)-O(1)	2.210(6)	C(12)-C(13)	1.379(11)
F(1)-C(26)	1.380(12)	C(13)-C(14)	1.369(12)
F(2)-C(26)	1.322(12)	C(14)-C(15)	1.387(11)
F(3)-C(26)	1.296(10)	C(15)-C(16)	1.404(10)
N(1)-C(1)	1.336(9)	C(17)-C(19)	1.498(12)
N(1)-C(5)	1.362(9)	C(17)-C(18)	1.508(11)
N(2)-C(10)	1.352(9)	C(17)-C(20)	1.518(12)
N(2)-C(6)	1.356(9)	C(21)-C(22)	1.499(13)
O(1)-C(25)	1.190(9)	C(21)-C(24)	1.530(11)
O(2)-C(25)	1.242(10)	C(21)-C(23)	1.535(12)
C(1)-C(2)	1.369(10)	C(25)-C(26)	1.532(12)
C(2)-C(3)	1.389(10)	C(27)-C(28)	1.412(12)
C(3)-C(4)	1.397(10)	C(29)-C(30A)	1.369(15)
C(3)-C(17)	1.526(10)	C(29)-C(30)	1.385(15)
C(4)-C(5)	1.377(10)	C(31)-C(32)	1.338(8)
C(5)-C(6)	1.470(10)	C(31)-C(33)#1	1.343(8)
C(6)-C(7)	1.375(10)	C(32)-C(33)	1.359(8)
C(7)-C(8)	1.399(10)	C(33)-C(31)#1	1.343(8)

N(2)-Ir(1)-C(16)	78.8(3)	C(4)-C(5)-C(6)	122.9(7)
N(2)-Ir(1)-C(29)	90.9(4)	N(2)-C(6)-C(7)	120.6(7)
C(16)-Ir(1)-C(29)	89.5(4)	N(2)-C(6)-C(5)	113.8(6)
N(2)-Ir(1)-N(1)	76.7(2)	C(7)-C(6)-C(5)	125.5(7)
C(16)-Ir(1)-N(1)	155.4(3)	C(6)-C(7)-C(8)	120.6(7)
C(29)-Ir(1)-N(1)	89.5(3)	C(9)-C(8)-C(7)	116.6(7)
N(2)-Ir(1)-C(27)	161.0(3)	C(9)-C(8)-C(21)	123.4(7)
C(16)-Ir(1)-C(27)	120.2(3)	C(7)-C(8)-C(21)	119.9(7)
C(29)-Ir(1)-C(27)	89.6(5)	C(10)-C(9)-C(8)	122.0(7)
N(1)-Ir(1)-C(27)	84.3(3)	N(2)-C(10)-C(9)	119.5(7)
N(2)-Ir(1)-C(28)	161.0(3)	N(2)-C(10)-C(11)	112.1(6)
C(16)-Ir(1)-C(28)	82.2(3)	C(9)-C(10)-C(11)	128.4(7)
C(29)-Ir(1)-C(28)	90.1(4)	C(16)-C(11)-C(12)	121.5(7)
N(1)-Ir(1)-C(28)	122.3(3)	C(16)-C(11)-C(10)	117.0(6)
C(27)-Ir(1)-C(28)	38.0(3)	C(12)-C(11)-C(10)	121.5(7)
N(2)-Ir(1)-O(1)	97.6(2)	C(13)-C(12)-C(11)	120.2(8)
C(16)-Ir(1)-O(1)	95.1(2)	C(14)-C(13)-C(12)	119.4(8)
C(29)-Ir(1)-O(1)	170.9(4)	C(13)-C(14)-C(15)	120.8(8)
N(1)-Ir(1)-O(1)	89.5(2)	C(14)-C(15)-C(16)	121.9(8)
C(27)-Ir(1)-O(1)	81.3(3)	C(11)-C(16)-C(15)	116.2(7)
C(28)-Ir(1)-O(1)	82.9(3)	C(11)-C(16)-Ir(1)	112.6(5)
C(1)-N(1)-C(5)	116.5(6)	C(15)-C(16)-Ir(1)	131.2(6)
C(1)-N(1)-Ir(1)	128.8(5)	C(19)-C(17)-C(18)	108.1(8)
C(5)-N(1)-Ir(1)	113.9(5)	C(19)-C(17)-C(20)	110.5(8)
C(10)-N(2)-C(6)	120.6(6)	C(18)-C(17)-C(20)	108.7(8)
C(10)-N(2)-Ir(1)	119.4(5)	C(19)-C(17)-C(3)	108.6(7)
C(6)-N(2)-Ir(1)	120.0(5)	C(18)-C(17)-C(3)	111.6(6)
C(25)-O(1)-Ir(1)	127.2(6)	C(20)-C(17)-C(3)	109.3(7)
N(1)-C(1)-C(2)	123.6(7)	C(22)-C(21)-C(24)	111.1(9)
C(1)-C(2)-C(3)	121.4(7)	C(22)-C(21)-C(8)	108.1(7)
C(2)-C(3)-C(4)	114.7(7)	C(24)-C(21)-C(8)	111.9(7)
C(2)-C(3)-C(17)	124.2(7)	C(22)-C(21)-C(23)	109.4(8)
C(4)-C(3)-C(17)	121.1(7)	C(24)-C(21)-C(23)	106.7(8)
C(5)-C(4)-C(3)	121.6(7)	C(8)-C(21)-C(23)	109.5(7)
N(1)-C(5)-C(4)	122.1(7)	O(1)-C(25)-O(2)	130.1(10)
N(1)-C(5)-C(6)	115.0(6)	O(1)-C(25)-C(26)	119.6(9)

O(2)-C(25)-C(26)	110.1(8)	C(27)-C(28)-Ir(1)	70.9(4)
F(3)-C(26)-F(2)	107.4(9)	C(30A)-C(29)-C(30)	89.4(14)
F(3)-C(26)-F(1)	106.4(9)	C(30A)-C(29)-Ir(1)	123.7(11)
F(2)-C(26)-F(1)	101.5(8)	C(30)-C(29)-Ir(1)	120.9(10)
F(3)-C(26)-C(25)	115.8(8)	C(32)-C(31)-C(33)#1	119.4(4)
F(2)-C(26)-C(25)	114.3(9)	C(31)-C(32)-C(33)	120.2(4)
F(1)-C(26)-C(25)	110.2(8)	C(31)#1-C(33)-C(32)	120.3(4)
C(28)-C(27)-Ir(1)	71.1(5)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,-z+1

Table 13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-TFA**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	30(1)	29(1)	26(1)	0(1)	1(1)	-6(1)
F(1)	49(3)	128(7)	149(7)	59(6)	6(4)	9(4)
F(2)	80(4)	80(4)	90(5)	-11(4)	36(4)	12(4)
F(3)	72(4)	62(4)	185(8)	-32(5)	55(5)	-35(3)
N(1)	30(3)	31(3)	21(3)	-1(2)	-1(2)	0(3)
N(2)	28(3)	23(3)	30(3)	-5(2)	10(2)	-2(2)
O(1)	41(3)	47(4)	62(4)	-7(3)	5(3)	-5(3)
O(2)	61(4)	69(5)	83(5)	23(4)	10(4)	8(4)
C(1)	33(4)	30(4)	30(4)	3(3)	0(3)	11(3)
C(2)	43(4)	27(4)	31(4)	-2(3)	3(3)	7(3)
C(3)	35(4)	31(4)	29(4)	-7(3)	3(3)	3(3)
C(4)	35(4)	27(4)	24(4)	-4(3)	3(3)	8(3)
C(5)	28(4)	32(4)	28(4)	0(3)	5(3)	8(3)
C(6)	28(4)	28(4)	29(4)	-6(3)	3(3)	4(3)
C(7)	44(4)	37(4)	29(4)	-9(3)	-6(3)	10(4)
C(8)	40(4)	27(4)	34(4)	-10(3)	-1(3)	10(3)
C(9)	44(4)	24(4)	39(4)	-6(4)	3(3)	5(4)
C(10)	32(4)	28(4)	29(4)	2(3)	10(3)	-5(3)
C(11)	34(4)	27(4)	33(4)	-6(3)	6(3)	-10(3)
C(12)	47(5)	34(4)	39(5)	-9(4)	7(4)	-4(4)
C(13)	53(5)	36(5)	44(5)	-15(4)	3(4)	-8(4)
C(14)	51(5)	55(5)	30(4)	-10(4)	1(3)	-14(5)
C(15)	48(5)	44(5)	41(5)	-5(4)	4(4)	-19(4)
C(16)	41(4)	25(4)	31(4)	-2(3)	7(3)	-10(3)
C(17)	49(4)	27(4)	37(4)	-2(4)	-12(3)	7(4)
C(18)	147(11)	25(5)	83(8)	-12(5)	-63(8)	11(6)
C(19)	88(7)	51(6)	40(5)	-6(4)	-5(5)	-4(5)
C(20)	55(6)	73(8)	85(8)	-8(6)	-10(5)	-2(6)
C(21)	56(5)	29(4)	40(5)	-4(3)	-7(4)	15(4)
C(22)	87(8)	63(7)	75(8)	23(6)	-8(6)	12(6)
C(23)	76(7)	47(6)	79(7)	3(5)	-32(6)	12(5)
C(24)	148(11)	40(6)	67(7)	-18(5)	-37(7)	46(7)
C(25)	67(6)	32(5)	50(5)	16(4)	3(5)	-8(4)
C(26)	44(5)	45(6)	90(8)	-4(5)	20(5)	-3(4)
C(27)	73(6)	35(5)	38(5)	11(4)	-30(4)	-2(4)
C(28)	81(7)	36(5)	35(5)	2(4)	-27(4)	-12(4)
C(29)	79(9)	127(13)	61(8)	-18(7)	24(6)	-61(9)
C(30)	55(12)	63(14)	35(11)	-7(9)	22(9)	-18(10)
C(30A)	27(8)	52(11)	102(16)	-10(10)	25(9)	0(7)
C(31)	68(6)	53(5)	23(4)	2(4)	23(4)	-15(5)
C(32)	198(19)	121(14)	173(18)	-99(14)	137(17)	-108(14)
C(33)	123(12)	103(11)	84(10)	9(8)	0(8)	-47(10)

Table 14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1-TFA**.

	x	y	z	U(eq)
H(1)	2081	-934	2454	37
H(2)	1641	-1850	1676	41
H(4)	903	579	906	35
H(7)	906	2171	948	44
H(9)	1038	4383	2147	43
H(12)	1423	4796	3073	48
H(13)	1748	5106	4083	53
H(14)	2139	3848	4694	55
H(15)	2224	2291	4309	53
H(18A)	1437	-2526	759	129
H(18B)	732	-2759	431	129
H(18C)	780	-2646	1158	129
H(19A)	970	-323	47	89
H(19B)	826	-1380	-226	89
H(19C)	1542	-1134	76	89
H(20A)	-80	-1363	1160	107
H(20B)	-170	-1568	444	107
H(20C)	-33	-489	683	107
H(22A)	1513	4494	649	112
H(22B)	917	4586	152	112
H(22C)	1225	3545	315	112
H(23A)	85	2998	491	102
H(23B)	-251	4045	420	102
H(23C)	-338	3442	1037	102
H(24A)	136	4944	1601	129
H(24B)	131	5397	928	129
H(24C)	803	5422	1340	129
H(31)	3065	6051	4922	57
H(32)	2438	6625	4110	195
H(33)	1950	8136	4164	124

Table 15. Crystal data and structure refinement for **1-TFA$_2$**.

Identification code	irx2xm	
Empirical formula	C31 H31 F6 Ir N2 O5	
Formula weight	817.78	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8262(9) Å	α= 60.8400(10)°.
	b = 12.8751(10) Å	β= 70.9100(10)°.
	c = 13.0574(10) Å	γ = 67.3880(10)°.
Volume	1578.5(2) Å^3	
Z	2	
Density (calculated)	1.721 Mg/m^3	
Absorption coefficient	4.306 mm^{-1}	
F(000)	804	
Crystal size	0.10 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.81 to 24.54°.	
Index ranges	-15<=h<=15, -16<=k<=7, -16<=l<=13	
Reflections collected	6926	
Independent reflections	4844 [R(int) = 0.0227]	
Completeness to theta = 24.54°	92.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.806 and 0.646	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4844 / 0 / 414	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1312	
R indices (all data)	R1 = 0.0631, wR2 = 0.1341	
Largest diff. peak and hole	3.420 and -1.342 e.Å^{-3}	

Table 16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1-TFA$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	2857(1)	1384(1)	2195(1)	37(1)
N(1)	2708(7)	2105(7)	331(7)	37(2)
N(2)	983(7)	2000(7)	2228(7)	37(2)
O(1)	3088(6)	3005(6)	1923(7)	43(2)
O(2)	1289(7)	4394(7)	1435(9)	62(2)
O(3)	2768(8)	-347(7)	2644(8)	57(2)
F(1)	3905(6)	5004(7)	1115(9)	78(2)
F(2)	2033(6)	6083(6)	1403(6)	52(2)
F(3)	2903(10)	4613(8)	2867(7)	89(3)
F(4)	3188(16)	-2781(9)	3721(10)	137(5)
F(5)	3665(9)	-2788(12)	2021(11)	113(4)
F(6)	1849(7)	-2348(11)	2788(10)	99(3)
C(13)	-1035(9)	2208(9)	3320(9)	41(2)
C(14)	232(9)	1831(8)	3268(9)	38(2)
C(25)	4675(8)	545(10)	2756(10)	46(2)
C(11)	-731(8)	2975(9)	1221(10)	42(2)
C(26)	4836(9)	903(10)	1568(10)	47(2)
C(1)	3598(9)	2080(9)	-610(10)	45(2)
C(12)	-1556(9)	2805(9)	2292(10)	42(2)
C(10)	549(8)	2551(9)	1180(9)	38(2)
C(15)	-2968(9)	3301(9)	2301(9)	42(2)
C(5)	1501(8)	2640(8)	110(9)	37(2)
C(27)	2300(9)	4023(9)	1709(9)	42(2)
C(19)	911(9)	1268(9)	4269(8)	39(2)
C(30)	2855(11)	-2199(10)	2693(10)	51(3)
C(17)	-3300(10)	2720(10)	1686(10)	50(3)
C(18)	-3255(10)	4703(10)	1609(12)	54(3)
C(23)	2830(10)	652(10)	4897(10)	47(2)
C(4)	1226(9)	3151(9)	-1002(9)	40(2)
C(16)	-3716(11)	2992(13)	3544(11)	56(3)
C(6)	1854(11)	3690(11)	-3217(10)	51(2)
C(9)	801(13)	3234(15)	-3187(12)	69(4)
C(8)	1378(17)	5110(14)	-3649(14)	77(4)
C(7)	2996(15)	3370(20)	-4137(14)	112(8)
C(24)	2212(9)	1044(9)	3968(9)	39(2)
C(2)	3379(10)	2524(10)	-1731(9)	44(2)
C(21)	923(12)	685(11)	6295(11)	56(3)
C(22)	2181(11)	485(11)	6051(10)	52(3)
C(28)	2797(10)	4947(10)	1767(10)	48(2)
C(20)	269(11)	1094(11)	5421(10)	51(2)
C(3)	2162(9)	3116(9)	-1987(9)	43(2)
O(4)	3654(15)	-584(13)	1024(12)	113(5)
O(5)	1524(14)	9933(10)	9555(12)	113(5)
C(35)	770(30)	9375(19)	9710(20)	149(12)
C(29)	2850(30)	-820(20)	2133(15)	161(14)

Table 17. Bond lengths [Å] and angles [°] for **1-TFA$_2$**.

Ir(1)-N(2)	2.039(7)	C(11)-C(10)	1.391(12)
Ir(1)-O(3)	2.047(7)	C(1)-C(2)	1.361(15)
Ir(1)-O(1)	2.053(6)	C(12)-C(15)	1.539(12)
Ir(1)-C(24)	2.060(10)	C(10)-C(5)	1.465(14)
Ir(1)-C(26)	2.158(10)	C(15)-C(16)	1.509(16)
Ir(1)-N(1)	2.184(8)	C(15)-C(18)	1.526(14)
Ir(1)-C(25)	2.191(8)	C(15)-C(17)	1.542(12)
N(1)-C(1)	1.337(13)	C(5)-C(4)	1.363(13)
N(1)-C(5)	1.384(11)	C(27)-C(28)	1.556(11)
N(2)-C(14)	1.324(13)	C(19)-C(20)	1.395(15)
N(2)-C(10)	1.368(12)	C(19)-C(24)	1.407(14)
O(1)-C(27)	1.240(12)	C(30)-C(29)	1.55(2)
O(2)-C(27)	1.207(12)	C(23)-C(24)	1.400(13)
O(3)-C(29)	1.065(18)	C(23)-C(22)	1.401(16)
F(1)-C(28)	1.316(14)	C(4)-C(3)	1.403(14)
F(2)-C(28)	1.330(13)	C(6)-C(3)	1.509(15)
F(3)-C(28)	1.319(13)	C(6)-C(8)	1.55(2)
F(4)-C(30)	1.287(15)	C(6)-C(9)	1.551(15)
F(5)-C(30)	1.343(14)	C(6)-C(7)	1.557(19)
F(6)-C(30)	1.235(13)	C(2)-C(3)	1.411(14)
C(13)-C(14)	1.375(13)	C(21)-C(22)	1.362(17)
C(13)-C(12)	1.394(14)	C(21)-C(20)	1.362(15)
C(14)-C(19)	1.481(12)	O(4)-C(29)	1.41(3)
C(25)-C(26)	1.354(16)	O(5)-C(35)	1.26(3)
C(11)-C(12)	1.389(15)		

N(2)-Ir(1)-O(3)	88.5(3)	C(12)-C(11)-C(10)	121.6(9)
N(2)-Ir(1)-O(1)	96.8(3)	C(25)-C(26)-Ir(1)	73.2(6)
O(3)-Ir(1)-O(1)	172.2(3)	N(1)-C(1)-C(2)	124.2(9)
N(2)-Ir(1)-C(24)	79.3(3)	C(11)-C(12)-C(13)	116.6(9)
O(3)-Ir(1)-C(24)	87.0(3)	C(11)-C(12)-C(15)	120.1(9)
O(1)-Ir(1)-C(24)	88.3(3)	C(13)-C(12)-C(15)	123.2(9)
N(2)-Ir(1)-C(26)	161.5(4)	N(2)-C(10)-C(11)	118.0(9)
O(3)-Ir(1)-C(26)	91.8(4)	N(2)-C(10)-C(5)	115.8(8)
O(1)-Ir(1)-C(26)	85.0(3)	C(11)-C(10)-C(5)	126.2(9)
C(24)-Ir(1)-C(26)	119.2(4)	C(16)-C(15)-C(18)	109.3(9)
N(2)-Ir(1)-N(1)	76.8(3)	C(16)-C(15)-C(12)	112.7(9)
O(3)-Ir(1)-N(1)	95.2(3)	C(18)-C(15)-C(12)	107.0(7)
O(1)-Ir(1)-N(1)	91.6(3)	C(16)-C(15)-C(17)	108.9(8)
C(24)-Ir(1)-N(1)	155.9(3)	C(18)-C(15)-C(17)	110.9(8)
C(26)-Ir(1)-N(1)	84.8(3)	C(12)-C(15)-C(17)	108.0(8)
N(2)-Ir(1)-C(25)	162.2(4)	C(4)-C(5)-N(1)	122.6(9)
O(3)-Ir(1)-C(25)	88.8(4)	C(4)-C(5)-C(10)	123.2(8)
O(1)-Ir(1)-C(25)	84.5(3)	N(1)-C(5)-C(10)	114.1(8)
C(24)-Ir(1)-C(25)	82.9(4)	O(2)-C(27)-O(1)	131.5(8)
C(26)-Ir(1)-C(25)	36.3(4)	O(2)-C(27)-C(28)	118.2(9)
N(1)-Ir(1)-C(25)	121.0(4)	O(1)-C(27)-C(28)	110.2(8)
C(1)-N(1)-C(5)	115.9(8)	C(20)-C(19)-C(24)	122.6(8)
C(1)-N(1)-Ir(1)	129.8(7)	C(20)-C(19)-C(14)	120.8(9)
C(5)-N(1)-Ir(1)	114.3(6)	C(24)-C(19)-C(14)	116.3(8)
C(14)-N(2)-C(10)	122.4(8)	F(6)-C(30)-F(4)	109.2(12)
C(14)-N(2)-Ir(1)	118.6(6)	F(6)-C(30)-F(5)	104.3(8)
C(10)-N(2)-Ir(1)	119.0(6)	F(4)-C(30)-F(5)	106.5(13)
C(27)-O(1)-Ir(1)	127.2(5)	F(6)-C(30)-C(29)	114.0(17)
C(29)-O(3)-Ir(1)	133.2(11)	F(4)-C(30)-C(29)	110.8(10)
C(14)-C(13)-C(12)	121.4(9)	F(5)-C(30)-C(29)	111.6(13)
N(2)-C(14)-C(13)	119.8(8)	C(24)-C(23)-C(22)	121.4(9)
N(2)-C(14)-C(19)	112.7(8)	C(5)-C(4)-C(3)	121.3(9)
C(13)-C(14)-C(19)	127.4(9)	C(3)-C(6)-C(8)	109.4(9)
C(26)-C(25)-Ir(1)	70.5(6)	C(3)-C(6)-C(9)	110.2(9)

C(8)-C(6)-C(9)	107.6(11)	F(3)-C(28)-F(2)	107.5(9)
C(3)-C(6)-C(7)	112.5(11)	F(1)-C(28)-C(27)	112.6(9)
C(8)-C(6)-C(7)	108.8(13)	F(3)-C(28)-C(27)	110.8(9)
C(9)-C(6)-C(7)	108.2(10)	F(2)-C(28)-C(27)	111.4(7)
C(23)-C(24)-C(19)	115.8(9)	C(21)-C(20)-C(19)	119.0(10)
C(23)-C(24)-Ir(1)	131.7(8)	C(4)-C(3)-C(2)	114.9(9)
C(19)-C(24)-Ir(1)	112.5(6)	C(4)-C(3)-C(6)	121.2(9)
C(1)-C(2)-C(3)	120.9(10)	C(2)-C(3)-C(6)	123.9(9)
C(22)-C(21)-C(20)	121.1(11)	O(3)-C(29)-O(4)	119.6(18)
C(21)-C(22)-C(23)	120.0(10)	O(3)-C(29)-C(30)	123.4(15)
F(1)-C(28)-F(3)	106.4(9)	O(4)-C(29)-C(30)	107.6(17)
F(1)-C(28)-F(2)	107.8(9)		

Symmetry transformations used to generate equivalent atoms:

Table 18. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-TFA$_2$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	32(1)	28(1)	54(1)	-14(1)	-24(1)	0(1)
N(1)	32(4)	29(4)	49(5)	-9(4)	-18(3)	-6(3)
N(2)	35(4)	30(4)	48(5)	-15(4)	-22(3)	-1(3)
O(1)	34(3)	32(4)	63(5)	-16(3)	-28(3)	1(3)
O(2)	45(4)	37(4)	106(7)	-19(5)	-43(4)	-3(4)
O(3)	69(5)	39(4)	70(5)	-17(4)	-30(4)	-14(4)
F(1)	47(4)	45(4)	147(8)	-31(5)	-45(4)	-7(3)
F(2)	54(4)	36(3)	71(4)	-23(3)	-27(3)	-3(3)
F(3)	166(9)	57(5)	67(5)	-6(4)	-72(5)	-34(6)
F(4)	270(18)	43(5)	102(8)	-1(6)	-83(9)	-43(8)
F(5)	73(6)	156(10)	158(10)	-124(9)	36(6)	-45(7)
F(6)	58(5)	147(9)	139(8)	-98(8)	27(5)	-57(6)
C(13)	43(5)	34(5)	42(5)	-11(5)	-15(4)	-7(4)
C(14)	46(5)	24(4)	46(5)	-9(4)	-24(4)	-5(4)
C(25)	24(4)	42(6)	67(7)	-20(5)	-29(4)	9(4)
C(11)	35(5)	32(5)	63(6)	-17(5)	-24(4)	-3(4)
C(26)	40(5)	41(6)	62(7)	-18(5)	-21(5)	-7(5)
C(1)	37(5)	31(5)	62(7)	-12(5)	-15(5)	-8(4)
C(12)	37(5)	29(5)	66(7)	-19(5)	-25(5)	-3(4)
C(10)	38(5)	32(5)	50(5)	-15(5)	-24(4)	-4(4)
C(15)	36(5)	35(5)	51(6)	-9(5)	-19(4)	-9(4)
C(5)	34(5)	27(5)	51(6)	-13(4)	-22(4)	-1(4)
C(27)	51(6)	33(5)	43(5)	-8(5)	-22(4)	-13(5)
C(19)	41(5)	32(5)	43(5)	-8(4)	-20(4)	-8(4)
C(30)	67(7)	38(6)	49(6)	-14(5)	-15(5)	-17(5)
C(17)	48(6)	45(6)	61(7)	-14(5)	-26(5)	-15(5)
C(18)	46(6)	39(6)	83(8)	-19(6)	-31(6)	-9(5)
C(23)	46(6)	43(6)	50(6)	-13(5)	-24(5)	-8(5)
C(4)	36(5)	30(5)	56(6)	-12(5)	-22(4)	-6(4)
C(16)	38(6)	59(7)	67(7)	-26(7)	-9(5)	-8(5)
C(6)	52(6)	54(7)	45(6)	-17(6)	-14(5)	-14(6)
C(9)	73(9)	84(10)	70(8)	-36(8)	-24(7)	-23(8)
C(8)	110(12)	59(9)	65(8)	-11(7)	-49(8)	-16(9)
C(7)	65(10)	220(30)	65(9)	-81(14)	7(8)	-32(14)
C(24)	45(5)	29(5)	44(5)	-7(4)	-19(4)	-12(4)
C(2)	42(5)	32(5)	45(6)	-5(5)	-12(4)	-7(4)
C(21)	68(8)	54(7)	52(7)	-23(6)	-17(5)	-17(6)
C(22)	63(7)	47(6)	45(6)	-13(5)	-24(5)	-12(6)
C(28)	57(6)	36(5)	55(6)	-10(5)	-34(5)	-8(5)
C(20)	52(6)	49(6)	59(7)	-24(6)	-17(5)	-12(5)
C(3)	46(5)	31(5)	53(6)	-13(5)	-16(5)	-9(4)
O(4)	157(14)	84(9)	95(9)	-45(8)	3(9)	-39(10)
O(5)	185(13)	44(5)	144(10)	-1(6)	-127(10)	-33(7)
C(35)	270(30)	59(11)	120(17)	-13(12)	-140(20)	15(17)
C(29)	380(40)	94(15)	51(9)	3(10)	-49(16)	-140(20)

Table 19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **1-TFA$_2$**.

	x	y	z	U(eq)
H(13)	-1567	2059	4073	49
H(25A)	4934	1016	3012	55
H(25B)	4889	-357	3254	55
H(11)	-1049	3390	499	50
H(26A)	5165	232	1292	56
H(26B)	5209	1602	1051	56
H(1)	4437	1730	-489	54
H(17A)	-2949	1821	2040	74
H(17B)	-2955	3053	834	74
H(17C)	-4206	2916	1793	74
H(18A)	-4110	5038	1459	82
H(18B)	-2678	4907	849	82
H(18C)	-3159	5064	2075	82
H(23)	3709	496	4741	56
H(4)	384	3538	-1111	49
H(16A)	-3579	3430	3911	85
H(16B)	-3455	2098	4021	85
H(16C)	-4602	3245	3506	85
H(9A)	879	2379	-2590	104
H(9B)	867	3272	-3972	104
H(9C)	-8	3763	-2981	104
H(8A)	613	5322	-3115	116
H(8B)	1205	5486	-4458	116
H(8C)	2012	5423	-3646	116
H(7A)	2824	3931	-4945	168
H(7B)	3152	2517	-4007	168
H(7C)	3729	3472	-4037	168
H(2)	4056	2433	-2348	53
H(21)	495	537	7087	67
H(22)	2618	232	6665	62
H(20)	-611	1257	5594	61

DFT section:

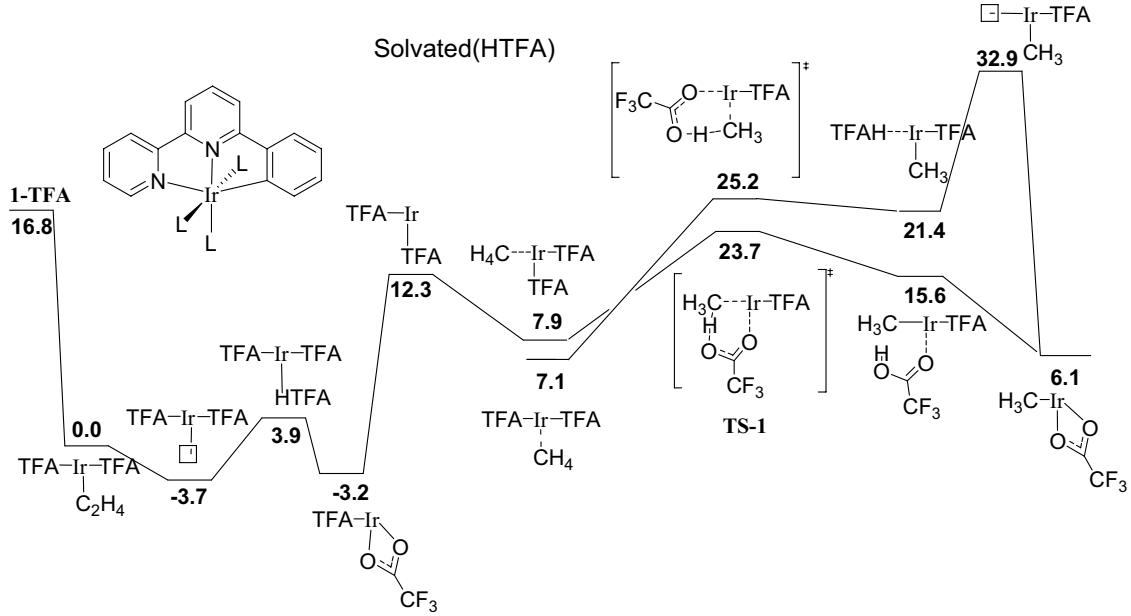


Figure S39. B3LYP free energy surface (at 453K) for the proposed pathway for the activation of methane by **1-TFA**.

Table 20. Comparisoin of DFT electronic energies and free energies of solvation. Grid 1 = default Jaguar grid settings. Grid 2 = ultra-fine grid (options set to -14).

	ΔΔE/LACV3P++**					
Transition State	B3LYP/grid 1	B3LYP/grid 2	M06/grid 2	M06-2X/grid 2	MPW1K/grid 2	bp86/grid 2
cis	0.5	0.7	0.3	1.2	1	0
trans	0	0	0	0	0	0.2
OHM	5.8	1.8	0.5	1.6	4.2	0.8

	ΔΔG(solv)/LACV3P++**					
	B3LYP/grid 1	B3LYP/grid 2	M06/grid 2	M06-2X/grid 2	MPW1K/grid 2	bp86/grid 2
cis		3.4	3.5	3.4	3.3	3.2
trans		5	5.4	5.1	5.1	4.7
OHM		0	0	0	0	0

DFT Calculations: All calculations were carried out using the B3LYP density functional as implemented by the Jaguar 7.0 program packages.[9,10,11,12] Geometries were optimized using the LACVP** basis set. The LACV3P++** basis set was used for more electronic energies. Free energy corrections were performed using a fixed value of 3KT for Hrot/trans, 30 eU for Srot/trans, and Poisson-Boltzman salvation energies (ε = 8.42 and solvent radius = 2.479 Å) for all solution phase species (the pV term was also neglected). Gas phase corrections were used for ethylene and ethane.

DFT B3LYP/LACVP geometries**

```
1-TFA
Gas phase Energy:  -1514.64688731370 hartrees
Solvation Energy:  -1514.65933957352 hartrees
Zero Point Energy:  238.963 kcal/mol
Coordinates:
  Ir1           0.2247001228      0.9377390404      0.3896920414
  C2           -3.3964145570      3.4063290774     -1.5680718193
  C3           -3.5234510441      2.9021209705     -0.2742949345
  C4           -2.4722271296      2.1673520308      0.2674384369
  N5           -1.3569714424      1.9258387056     -0.4571567141
  C6           -1.2060024318      2.4075816061     -1.7150048806
  C7           -2.2382580085      3.1640225540     -2.2901848192
  H8           -4.1993827976      3.9929290709     -2.0037974576
  H9           -4.4166464866      3.0995333429      0.3041559133
  H10          -2.1225145250      3.5588961189     -3.2919097818
  C11          -2.3105726126      0.4841239271      4.1321561417
  C12          -1.2710936450      0.4006787573      3.2118544609
  N13          -1.3314780756      0.9393569828      1.9847949525
  C14          -2.4641681290      1.5975518099      1.6230771222
  C15          -3.5488764811      1.7094982496      2.4955004441
  C16          -3.4743146361      1.1533304914      3.7661561395
  H17          -2.1973531989      0.0319195120      5.1112631206
  H18          -0.3548864690     -0.1125717071      3.4681818218
  H19          -4.4415163165      2.2380284410      2.1852237233
  H20          -4.3088108046      1.2429243358      4.4546251511
  C21           2.5002024343      1.3288189916     -3.4313415226
  C22           1.6031357266      2.0711419966     -4.2013829836
  C23           0.3852750779      2.4307336070     -3.6410848856
  C24           0.0686613525      2.0554074435     -2.3247579027
  C25           0.9730979517      1.3043170655     -1.5123865812
  C26           2.1885707399      0.9576915868     -2.1214709348
  H27           3.4595883060      1.0352708994     -3.8504822955
  H28           1.8505605319      2.3626231740     -5.2175369099
  H29          -0.3225665665      3.0064650476     -4.2307089015
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[12] Jaguar 6.0, Schrodinger, LLC, Portland, Oregon, 2005

H30	2.9343102186	0.3893018227	-1.5809320350
C39	-0.4251990254	-0.9813006078	-0.2115952893
H40	0.4007751977	-1.4615907376	-0.7511549034
H41	-0.5828288287	-1.5672115779	0.7064322864
C42	-1.6880285348	-1.0696973746	-1.0715189294
H43	-2.5673652064	-0.6577877044	-0.5618921550
H44	-1.5730543890	-0.5300584662	-2.0175756248
H45	-1.9238317873	-2.1136690788	-1.3198781529
C46	1.5246424626	0.0171917636	1.8970444432
C47	2.2608089411	0.1508822475	0.7237205731
H48	1.6363855044	0.7548626209	2.6867056957
H49	2.9349894148	0.9914459507	0.6022230663
H50	2.4362829744	-0.7174211140	0.0985314882
H51	1.1360931031	-0.9577023685	2.1793941212
C45	0.5102496850	3.7911143489	1.6191351994
O46	1.1707289676	2.8090234537	1.1292321329
O47	-0.7006534316	3.9383155189	1.7721398131
C48	1.4578131166	4.9348643906	2.0778156389
F49	0.7838301719	5.9660004945	2.6142192250
F50	2.3296938474	4.4899679011	3.0131877338
F51	2.1825815946	5.4140446877	1.0436915435

1-TFA2
Gas phase Energy: -1961.62691712553 hartrees
Solvation Energy: -1961.64209965221 hartrees
Zero Point Energy: 216.030 kcal/mol
Coordinates:

Ir1	0.2774103536	0.9958772405	0.2878813408
C2	-3.3820149890	3.3271931810	-1.7529969406
C3	-3.5196877455	2.8225616335	-0.4602937286
C4	-2.4503241642	2.1451233037	0.1153611581
N5	-1.3004814140	1.9828104102	-0.5724617678
C6	-1.1366918329	2.4594959272	-1.8264821003
C7	-2.1926809751	3.1481802578	-2.4411304934
H8	-4.2063248948	3.8593261477	-2.2176836304
H9	-4.4450206145	2.9600840104	0.0834209882
H10	-2.0733393915	3.5355312413	-3.4451405462
C11	-2.3531670555	0.4341740729	3.9741111354
C12	-1.2793452404	0.4016091406	3.0903268540
N13	-1.3209653543	0.9483998396	1.8678199364
C14	-2.4625312516	1.5641011522	1.4676269534
C15	-3.5770049710	1.6319599183	2.3045661457
C16	-3.5265702371	1.0628149732	3.5711774508
H17	-2.2588727146	-0.0264906097	4.9511628966
H18	-0.3542104786	-0.0801029031	3.3753394444
H19	-4.4797086257	2.1253147042	1.9676255226
H20	-4.3892069814	1.1106723089	4.2284264096
C21	2.6871387599	1.5999007953	-3.4185652636
C22	1.7802509024	2.3049456627	-4.2094604895
C23	0.5238020399	2.5917208725	-3.6920960368
C24	0.1768937708	2.1781866972	-2.3960513612
C25	1.0902351350	1.4585310470	-1.5713516235
C26	2.3453032084	1.1877662154	-2.1273650724
H27	3.6754682349	1.3639790118	-3.8047346775
H28	2.0486822293	2.6242000253	-5.2116900217
H29	-0.1902292848	3.1389431667	-4.3003572514
H30	3.0961805001	0.6449215550	-1.5688754115
C31	1.5099930358	-0.0984540353	1.7626249449
C32	2.2817350811	0.0754969567	0.6236989368
H33	1.6418321080	0.5684415326	2.6096337847
H34	3.0081274752	0.8789077645	0.5821137590
H35	2.3805342260	-0.7360850349	-0.0879511714
H36	1.0150729758	-1.0495758493	1.9354844837
C38	0.5329099811	3.7278630313	1.5294801636
O39	1.1690080600	2.7021889824	1.0633056295

O40	-0.6659132260	3.9456641072	1.6036123050
C41	1.5434038198	4.7789560762	2.0619990611
F42	0.9164238760	5.8519359302	2.5625821369
F43	2.3045802091	4.2485726299	3.0454780451
F44	2.3708119709	5.1982365032	1.0839400337
C45	-1.4406636132	-1.3102123415	-0.6073936818
O46	-0.2327118795	-0.8846875303	-0.4252855696
O47	-2.5097814677	-0.7439962022	-0.4439854688
C48	-1.4137837323	-2.7849855380	-1.0906756021
F49	-2.6495053330	-3.2472335405	-1.3232487342
F50	-0.6985818365	-2.9166836876	-2.2252869854
F51	-0.8456251754	-3.5766514964	-0.1526863275

pypyph.TFA.vacant.TFA.
Gas phase Energy: -1882.98115062387 hartrees
Solvation Energy: -1883.00864168184 hartrees
Zero Point Energy: 180.458 kcal/mol
Coordinates:

Ir1	0.5357475901	0.7588890966	0.3264240831
C2	-2.9255650266	3.3926104444	-1.3805987674
C3	-3.0503227687	2.8385473033	-0.1055425053
C4	-2.0182605807	2.0558432374	0.3987781821
N5	-0.9165135744	1.8524571723	-0.3638699709
C6	-0.7511303367	2.3732426186	-1.6124943069
C7	-1.7830783626	3.1638569838	-2.1341073388
H8	-3.7266844876	4.0047187586	-1.7826633838
H9	-3.9405102420	3.0153590988	0.4841758294
H10	-1.6770317543	3.5896835175	-3.1246435475
C11	-1.8168847879	0.1281415315	4.1589858320
C12	-0.8069695760	0.0630822725	3.2024406302
N13	-0.8955234797	0.6817361076	2.0199163762
C14	-2.0049930665	1.4057108446	1.7239310054
C15	-3.0542736628	1.5126304213	2.6363702828
C16	-2.9598241758	0.8676079997	3.8662187949
H17	-1.7019812059	-0.3897154158	5.1046357482
H18	0.1041599830	-0.4994111978	3.3794654102
H19	-3.9359870894	2.0924283650	2.3926623627
H20	-3.7701910235	0.9437317761	4.5844938396
C21	2.9821080242	1.2434177998	-3.2708731777
C22	2.1352381414	2.0547091159	-4.0340582166
C23	0.9030159691	2.4431304434	-3.5199048345
C24	0.5196339236	2.0172895388	-2.2391417330
C25	1.3732032962	1.1919734320	-1.4552701495
C26	2.6047151433	0.8167032638	-1.9947050268
H27	3.9448418030	0.9417012735	-3.6754440060
H28	2.4380500217	2.3809147213	-5.0244288271
H29	0.2480122870	3.0738068280	-4.1153299254
H30	3.2805829963	0.1868469068	-1.4211547527
C31	1.1905647088	3.2969447695	1.7721829548
O32	1.6579744297	2.2222796760	1.2146572540
O33	0.0427924851	3.7080424650	1.8105787545
C34	2.3334225182	4.1017356874	2.4427035692
F35	1.8602958658	5.1854044423	3.0722565031
F36	2.9814908002	3.3428642549	3.3524943485
F37	3.2351523987	4.5096730782	1.5281839141
C38	-1.2906780593	-1.4517375503	-0.5360512243
O39	-0.0610619684	-1.0632537615	-0.3911771828
O40	-2.3224583169	-0.8220461559	-0.3719877219
C41	-1.3415568010	-2.9325179530	-0.9921866515
F42	-2.6050319198	-3.3640285272	-1.1018691776
F43	-0.7405862555	-3.0889564787	-2.1880763127
F44	-0.7068184005	-3.7270498276	-0.1035998670

pypyph.TFA.HTFA-rot.TFA.
Gas phase Energy: -2409.79744887940 hartrees

Solvation Energy: -2409.82010394252 hartrees
Zero Point Energy: 206.296 kcal/mol
Coordinates:

Ir1	0.1198417689	1.0507387352	0.1779151221
C2	-3.3856396032	3.4868854711	-1.7953549335
C3	-3.5372989478	2.9948977779	-0.4982906741
C4	-2.4932167245	2.2824350017	0.0813832085
N5	-1.3553371194	2.0794165229	-0.6217609468
C6	-1.1692892209	2.5467177046	-1.8856097831
C7	-2.2052733835	3.2679589868	-2.4927488698
H8	-4.1947893936	4.0432547718	-2.2582426250
H9	-4.4567751805	3.1648416327	0.0469085665
H10	-2.0776092665	3.6471758096	-3.4993751643
C11	-2.3623488596	0.6117289023	3.9681440490
C12	-1.3257187518	0.5036312482	3.0454809489
N13	-1.3910249154	1.0319257542	1.8188744999
C14	-2.5057746577	1.7098314007	1.4433271132
C15	-3.5839946125	1.8518256059	2.3170622720
C16	-3.5134069462	1.2979000979	3.5914905892
H17	-2.2616046066	0.1661249396	4.9517102970
H18	-0.4134031189	-0.0290483311	3.2857740161
H19	-4.4699394195	2.3929694632	2.0088775623
H20	-4.3465753661	1.4040640355	4.2794062793
C21	2.6792277897	1.5328609054	-3.3521177295
C22	1.8250892048	2.2662500884	-4.1818448940
C23	0.5556657781	2.6097700778	-3.7272970597
C24	0.1421440630	2.2166449960	-2.4455417406
C25	1.0008410290	1.4652477161	-1.5931688713
C26	2.2706642335	1.1397406389	-2.0746109485
H27	3.6724859786	1.2657629319	-3.7048361654
H28	2.1495215776	2.5681434245	-5.1730217335
H29	-0.1064892625	3.1831680729	-4.3706065121
H30	2.9557548831	0.5737163329	-1.4492239918
C31	0.5650935221	3.7040744835	1.5243811081
O32	1.1166270845	2.6351645974	1.0516351668
O33	-0.5998068624	4.0695394206	1.4947165941
C34	1.6306328369	4.5782605494	2.2386721784
F35	1.0991116524	5.7120943719	2.7147954531
F36	2.1675557387	3.9045759329	3.2837615378
F37	2.6392210498	4.9083411473	1.4072830697
C38	-1.6827913083	-1.1897262072	-0.7081432439
O39	-0.4617179758	-0.7788519975	-0.5940407231
O40	-2.7314154780	-0.6038997198	-0.4892853292
C41	-1.7239401555	-2.6775977246	-1.1516042649
F42	-2.9271237289	-3.0070028946	-1.6413045322
F43	-0.8015857400	-2.9632498625	-2.0885497267
F44	-1.4830309428	-3.4775243840	-0.0833344622
O45	1.8393500960	-0.0122243508	0.9751323469
C46	2.2328361391	-1.1091044529	1.3319618710
O47	3.5021490003	-1.3480592794	1.6156983659
F48	1.2906456855	-3.0280438585	0.3466610023
C49	1.3576442310	-2.3718310275	1.5039682684
F50	1.8925475846	-3.1763960102	2.4322639170
F51	0.1308039948	-2.0225885391	1.9061945551
H52	4.0037913592	-0.5252429550	1.4665825637

pypyph.TFA.ch4.TFA.
Gas phase Energy: -1923.51542665121 hartrees
Solvation Energy: -1923.53161513350 hartrees
Zero Point Energy: 210.115 kcal/mol
Coordinates:

Ir1	0.5739742487	0.7504293217	0.3776202278
C2	-2.8720595682	3.3213845426	-1.5147840088
C3	-3.0362075292	2.7879606206	-0.2356295319
C4	-2.0117911392	2.0279175614	0.3161992078

N5	-0.8804913196	1.8228825101	-0.3973674423
C6	-0.6812214904	2.3243254981	-1.6448624573
C7	-1.7002515332	3.0934614988	-2.2218305976
H8	-3.6652216775	3.9166052909	-1.9563629646
H9	-3.9493229748	2.9643787694	0.3179268482
H10	-1.5638114427	3.5032940407	-3.2153007347
C11	-1.9448810315	0.1684742238	4.1171316942
C12	-0.8941675331	0.1030655067	3.2062214182
N13	-0.9370731780	0.6991452213	2.0100387662
C14	-2.0426335526	1.4010289443	1.6529979389
C15	-3.1318298451	1.5070871849	2.5176369209
C16	-3.0839629584	0.8854148770	3.7616804257
H17	-1.8634924524	-0.3321355130	5.0755980032
H18	0.0143883619	-0.4433024304	3.4355848005
H19	-4.0102516257	2.0684390930	2.2245185068
H20	-3.9266220954	0.9615026691	4.4418620637
C21	3.1161122722	1.2265441441	-3.1778363375
C22	2.2804027019	2.0131594178	-3.9762885360
C23	1.0292708772	2.3867631593	-3.4969337952
C24	0.6161005640	1.9737488299	-2.2214430764
C25	1.4572960088	1.1723989017	-1.3981013543
C26	2.7084566223	0.8127034768	-1.9064612974
H27	4.0948521728	0.9326144662	-3.5486060277
H28	2.6038798627	2.3310278518	-4.9627000822
H29	0.3795935674	2.9985304678	-4.1172784658
H30	3.3846711256	0.2021861776	-1.3136650111
C31	1.0569281526	3.3736490248	1.7668372398
O32	1.5977774730	2.3151166384	1.2551838795
O33	-0.1112544838	3.7276535063	1.7827542765
C34	2.1424899909	4.2487468365	2.4475898368
F35	1.6110096440	5.3478643117	2.9991316314
F36	2.7628301220	3.5526886748	3.4277719579
F37	3.0822212443	4.6376736618	1.5638218157
C38	-1.2698457353	-1.4447823097	-0.5328480597
O39	-0.0407375435	-1.0809623204	-0.3553814385
O40	-2.3029248145	-0.8072479967	-0.4035539465
C41	-1.3291762564	-2.9385626452	-0.9482369424
F42	-2.5849533156	-3.3246921964	-1.2098316090
F43	-0.5818929657	-3.1787587472	-2.0425417841
F44	-0.8562527569	-3.7185540860	0.0518903376
H45	2.2224261636	-0.2037829639	0.7045000113
C46	2.3350568495	-0.7235085440	1.6983519060
H47	3.3370413220	-1.1427181445	1.5660723894
H48	2.3411602279	-0.0201694453	2.5281458976
H49	1.6154045055	-1.5303372345	1.8186821466

pypyph.TS.ch3-h-o-c-o-ir.TFA.
Gas phase Energy: -1923.49098422336 hartrees
Solvation Energy: -1923.50205187920 hartrees
Zero Point Energy: 207.875 kcal/mol
Coordinates:

Ir1	-0.2822805689	-0.0768431793	0.4186153651
H2	-0.4185102533	-0.1379925748	2.5519680584
O3	0.5299095338	-0.1086468878	3.3462030946
C4	1.5526166837	-0.3310257940	2.6424454873
C5	2.8888586902	-0.4670235744	3.3931664775
O6	1.5641646521	-0.4506563459	1.3919328231
F7	3.8952286361	-0.7566131138	2.5613689965
F8	3.1714626329	0.6831945574	4.0248302847
F9	2.7978114347	-1.4454089463	4.3094262068
C10	0.2966313668	-4.5185151691	-1.7841036628
C11	0.9071901720	-3.3447999993	-2.2183839613
C12	0.6739499911	-2.1524724050	-1.5304932825
N13	-0.1285870767	-2.1291511096	-0.4323648149
C14	-0.7155937905	-3.2579697788	-0.0211149150

C15	-0.5339394531	-4.4780393961	-0.6673233821
H16	0.4645597891	-5.4499928935	-2.3158720245
H17	1.5464579265	-3.3555429949	-3.0926348100
H18	-1.3531756671	-3.1680344973	0.8522515994
H19	-1.0354563182	-5.3662360571	-0.2986831702
C20	0.5837945567	4.6902449810	0.4187869389
C21	1.1143511009	3.8117025483	-0.5197718285
C22	0.8219681540	2.4416561142	-0.4441627136
C23	-0.0150529673	1.9237605396	0.5921743373
C24	-0.5354697019	2.8341834900	1.5169411895
C25	-0.2424101478	4.1983050074	1.4331817200
H26	0.8068323310	5.7513666192	0.3588274765
H27	1.7497162877	4.1977727643	-1.3128639141
H28	-1.1867817663	2.4807151706	2.3109793975
H29	-0.6645330037	4.8842755309	2.1635974526
C30	2.6154856425	0.6170049437	-3.2706999225
C31	2.2183635036	1.6885085512	-2.4804903761
C32	1.3392439722	1.4654220936	-1.4104217865
N33	0.8946187494	0.2030719988	-1.1963064129
C34	1.2657480943	-0.8566767658	-1.9430518065
C35	2.1473276042	-0.6721020727	-3.0057349807
H36	3.2999735647	0.7797411738	-4.0976281621
H37	2.5889175538	2.6869951257	-2.6796726429
H38	2.4644593658	-1.5056615220	-3.6193587687
C39	-2.2990382899	0.0177299716	-1.7837257251
O40	-2.0490594639	0.3481029866	-0.5577476482
C41	-3.7172504435	0.5079958466	-2.1820583832
F42	-4.0305218676	0.1309378496	-3.4301769675
F43	-4.6529394116	0.0006529377	-1.3508462084
F44	-3.7987585985	1.8525762400	-2.1221506460
O45	-1.6154765603	-0.5837672689	-2.5977842886
C46	-1.7571291707	-0.4785107756	2.1098660519
H47	-2.5854582809	-0.2832395630	1.4287028307
H48	-1.7997949005	-1.5244975224	2.4361208652
H49	-1.9770281544	0.1424072921	2.9907409966

pypyph.HTFA.ch3.TFA.
Gas phase Energy: -1923.49832386908 hartrees
Solvation Energy: -1923.50846358572 hartrees
Zero Point Energy: 210.777 kcal/mol
Coordinates:

Ir1	-0.3375404065	-0.0889638265	0.4284769493
H2	-0.1045816816	0.0977887479	2.9909355747
O3	0.7654323944	0.0398823008	3.4904809108
C4	1.6835903103	-0.2864808466	2.6354401064
C5	3.0755543474	-0.4715084438	3.2621705113
O6	1.5256101027	-0.4437428264	1.4230794594
F7	3.9697113746	-0.8128380330	2.3335918885
F8	3.4640998441	0.6706572931	3.8462062714
F9	3.0258078842	-1.4361442693	4.1941241289
C10	0.3059418147	-4.4966675155	-1.8459658711
C11	0.9104306782	-3.3133721486	-2.2618553034
C12	0.6722642533	-2.1308581020	-1.5583196160
N13	-0.1325212532	-2.1286101655	-0.4589959027
C14	-0.7141699179	-3.2673004081	-0.0661843707
C15	-0.5256361034	-4.4770738930	-0.7294281314
H16	0.4788636527	-5.4189284732	-2.3921548315
H17	1.5490680232	-3.3072773707	-3.1368060869
H18	-1.3531725522	-3.1915431982	0.8078786748
H19	-1.0230684080	-5.3732646261	-0.3746506815
C20	0.5102826779	4.6910015876	0.4524739936
C21	1.0620553116	3.8162072239	-0.4784286897
C22	0.7748193562	2.4442415260	-0.4185086734
C23	-0.0829736225	1.9162173588	0.6017396352
C24	-0.6286757319	2.8277662980	1.5125889708

C25	-0.3386901950	4.1931899583	1.4440430941
H26	0.7323130230	5.7529695803	0.4010927177
H27	1.7113308202	4.2091680737	-1.2570259447
H28	-1.3080541817	2.4730439866	2.2824515189
H29	-0.7824716019	4.8744302927	2.1663139425
C30	2.6202170120	0.6677230656	-3.2508372458
C31	2.2081930245	1.7289864666	-2.4512621210
C32	1.3175549797	1.4842302879	-1.3949396042
N33	0.8811019865	0.2186460981	-1.2044783337
C34	1.2650342781	-0.8280150225	-1.9569921706
C35	2.1589447565	-0.6290473630	-3.0093814924
H36	3.3123281762	0.8467685966	-4.0682641654
H37	2.5758662447	2.7314194448	-2.6376072601
H38	2.4897294755	-1.4516526436	-3.6309841336
C39	-2.3495133154	-0.0180184101	-1.7540882740
O40	-2.1030297787	0.2999820986	-0.5248179981
C41	-3.7874296023	0.4327733952	-2.1279213629
F42	-4.0857170679	0.1108087541	-3.3954537734
F43	-4.6991272535	-0.1610064481	-1.3271925385
F44	-3.9310985859	1.7668005685	-1.9950509067
O45	-1.6568268936	-0.5880010053	-2.5832217720
C46	-1.6650379273	-0.4720978082	2.0715795706
H47	-2.6565891503	-0.4340382393	1.6103127076
H48	-1.7504038986	0.2540669088	2.9025905322
H49	-1.5521180587	-1.4652185879	2.5347491677

pypyph.TFA-nochel.ch3.
Gas phase Energy: -1396.66971252843 hartrees
Solvation Energy: -1396.69124175349 hartrees
Zero Point Energy: 184.605 kcal/mol
Coordinates:

Ir1	-0.4064568888	-0.0547218681	0.4178791913
C10	0.3614159763	-4.4929899760	-1.8074691756
C11	0.9562341016	-3.3053963727	-2.2240049668
C12	0.7043906235	-2.1212915152	-1.5281621010
N13	-0.1119177253	-2.1195632193	-0.4350092216
C14	-0.6819056831	-3.2652854049	-0.0399545165
C15	-0.4750354804	-4.4768215140	-0.6941535168
H16	0.5463955464	-5.4149082870	-2.3502785541
H17	1.5986869039	-3.2965493481	-3.0964443409
H18	-1.3271373770	-3.1918021157	0.8298229913
H19	-0.9635876920	-5.3770042524	-0.3373270017
C20	0.5773523324	4.6856498768	0.5278374480
C21	1.1140114050	3.8161108427	-0.4186308325
C22	0.7826446749	2.4542256399	-0.3982616099
C23	-0.1095827606	1.9310468082	0.5993432945
C24	-0.6343549401	2.8381656215	1.5301987435
C25	-0.2951700364	4.1934952007	1.5022428181
H26	0.8348028457	5.7405997971	0.5030811254
H27	1.7894893943	4.2070697849	-1.1754644609
H28	-1.3243638304	2.4774941594	2.2867438720
H29	-0.7189974903	4.8714301949	2.2389948866
C30	2.6924456207	0.6699254380	-3.1878510012
C31	2.2559308477	1.7363738661	-2.4047939082
C32	1.3376250601	1.4953085518	-1.3734834326
N33	0.8902958779	0.2311253974	-1.1930350845
C34	1.3013432608	-0.8193215503	-1.9254085299
C35	2.2300257513	-0.6269290655	-2.9507649044
H36	3.4070432690	0.8465771774	-3.9862522565
H37	2.6284737616	2.7376920899	-2.5876325653
H38	2.5850250638	-1.4528373174	-3.5550721272
C39	-2.3194790793	-0.0602712801	-1.8084140726
O40	-2.1365622852	0.2301434125	-0.5539150956
C41	-3.7713333274	0.3297986233	-2.2056902168
F42	-4.0103049839	0.0167650142	-3.4863586547

F43	-4.6725834352	-0.3210274256	-1.4436725195
F44	-3.9746341187	1.6522482761	-2.0539841220
O45	-1.5704696052	-0.5546463298	-2.6302583977
C46	-1.5243784930	-0.3816105455	2.1493870445
H47	-2.3493126018	0.3302959738	2.2655871176
H48	-0.8690800699	-0.2751128613	3.0315356367
H49	-1.9616819529	-1.3911893142	2.1947359276

pypyph.ch4.TFA.TFA.
Gas phase Energy: -1923.51177311696 hartrees
Solvation Energy: -1923.52776615952 hartrees
Zero Point Energy: 210.098 kcal/mol
Coordinates:

Ir1	-0.2796102405	0.1010143125	0.4659756197
H2	-0.9698033415	-0.6306147985	2.1056008641
O3	0.9492840633	-1.9791296325	2.5761390716
C4	1.7044635811	-1.0453342593	2.3162236527
C5	3.1031493885	-0.9740759805	2.9771012843
O6	1.4925824305	-0.0321770772	1.5522387832
F7	4.0765363268	-0.8835827797	2.0531425239
F8	3.1855782669	0.1146519621	3.7747669269
F9	3.3450573191	-2.0555357762	3.7313685182
C10	-1.8476514546	-4.2894588966	-1.4238686851
C11	-2.4393352062	-3.0599968665	-1.7011451880
C12	-1.9210266373	-1.9040893098	-1.1111490361
N13	-0.8500632821	-1.9641873438	-0.2772070348
C14	-0.2813460137	-3.1474691317	-0.0108354206
C15	-0.7541008367	-4.3363517088	-0.5637109730
H16	-2.2396792048	-5.1964011131	-1.8743651804
H17	-3.2929603433	-3.0039167178	-2.3662138417
H18	0.5567773916	-3.1175952947	0.6731394641
H19	-0.2652796437	-5.2732235370	-0.3198715509
C20	-0.8712276286	4.8588570873	0.8817140450
C21	-1.6952166783	4.0581605210	0.0979751417
C22	-1.4602465775	2.6755851294	0.0262720988
C23	-0.3834640877	2.0868752759	0.7515088101
C24	0.4336542587	2.9100206961	1.5289224150
C25	0.1889480283	4.2843100573	1.5933102260
H26	-1.0491442187	5.9286215057	0.9379614016
H27	-2.5148724468	4.5117791386	-0.4534976540
H28	1.2643241843	2.4687460017	2.0711494675
H29	0.8333397072	4.9167374941	2.1990803694
C30	-4.0015331060	1.0514426885	-2.3039168498
C31	-3.3561108144	2.0676215632	-1.6085308176
C32	-2.2745206848	1.7553824119	-0.7743150096
N33	-1.8969468712	0.4496155920	-0.6655820264
C34	-2.4974252380	-0.5559930219	-1.3421105443
C35	-3.5773932643	-0.2725921514	-2.1789601430
H36	-4.8364521793	1.2885669954	-2.9561995411
H37	-3.6755762121	3.0973892781	-1.7152220642
H38	-4.0730770221	-1.0614252216	-2.7308164672
C39	1.7204655254	-0.3611168499	-1.5612925776
O40	0.8265325472	0.5073301268	-1.1686533143
C41	2.4711541568	0.1974248751	-2.7999669281
F42	3.4305670123	-0.6467094832	-3.1970916515
F43	1.6131574301	0.3650258003	-3.8317817363
F44	3.0393093487	1.3875433140	-2.5376877046
O45	1.9832893181	-1.4630862083	-1.1230381944
C46	-1.9502018292	-0.2079222023	2.4913288843
H47	-2.0826121297	0.8675055127	2.4101497993
H48	-1.8352359804	-0.4802570016	3.5440266316
H49	-2.7791924833	-0.7524339499	2.0419525654

pypyph.TS.TFA.ch3-h-o-c-o-ir.ef1.
Gas phase Energy: -1923.49015508957 hartrees

Solvation Energy: -1923.50388831089 hartrees
Zero Point Energy: 207.772 kcal/mol
Coordinates:

Ir1	-0.2716655291	-0.0561535702	0.4353291850
H2	-0.4425470307	-0.2151282258	2.4552577186
O3	0.5487036110	-0.2826165102	3.3483727750
C4	1.5659494869	-0.4754323524	2.6352650650
C5	2.9230153150	-0.5979478675	3.3497669193
O6	1.5765109004	-0.5145138801	1.3772176636
F7	3.7956644158	-1.3154325178	2.6351021247
F8	3.4290298239	0.6405798181	3.5249547247
F9	2.7845624759	-1.1695271741	4.5541260352
C10	-1.9568018200	-4.3081092079	-1.5050057725
C11	-2.5413457032	-3.0652091227	-1.7309667031
C12	-1.9741063599	-1.9280710341	-1.1495902252
N13	-0.8638117774	-2.0243271917	-0.3732784620
C14	-0.2880791876	-3.2157242704	-0.1774783573
C15	-0.8103118797	-4.3877705691	-0.7169869224
H16	-2.3890480539	-5.2011524794	-1.9458079024
H17	-3.4274870581	-2.9822177656	-2.3492283859
H18	0.6229131726	-3.2045348115	0.4082178436
H19	-0.3172073242	-5.3351365663	-0.5295157000
C20	-0.6359604667	4.7437178096	0.9393625517
C21	-1.5021462773	3.9837909440	0.1630667125
C22	-1.3309548919	2.5923046619	0.0828261144
C23	-0.2770613220	1.9357391989	0.7891704298
C24	0.5810439721	2.7295922023	1.5576613300
C25	0.4034160002	4.1131114263	1.6325775040
H26	-0.7633863298	5.8202027673	1.0033940421
H27	-2.3051059209	4.4756666359	-0.3803451709
H28	1.4074463402	2.2754178147	2.0957969883
H29	1.0851792546	4.7088928468	2.2344862744
C30	-3.9585127907	1.1252723628	-2.2561549773
C31	-3.2679254638	2.0999428622	-1.5472457795
C32	-2.1907030196	1.7301343339	-0.7274187063
N33	-1.8640122440	0.4103642126	-0.6531025523
C34	-2.5128006900	-0.5596479062	-1.3411706944
C35	-3.5866346539	-0.2182143891	-2.1616114884
H36	-4.7885845796	1.4088048901	-2.8959581766
H37	-3.5481602772	3.1432663429	-1.6301067859
H38	-4.1158144792	-0.9758662526	-2.7261611228
C39	1.6651403628	-0.5026063744	-1.7695676135
O40	0.8613224000	0.3745444588	-1.2564805093
C41	2.4154281855	0.1081394202	-2.9842803143
F42	3.3378935784	-0.7372275439	-3.4657142463
F43	1.5447822740	0.3789627145	-3.9854576467
F44	3.0361119769	1.2584065958	-2.6605453085
O45	1.8682321016	-1.6641326955	-1.4560498790
C46	-1.7698013689	-0.4998683989	2.1279546252
H47	-2.6284381811	-0.1908013641	1.5329309611
H48	-1.8303505023	-1.5731887986	2.3225156701
H49	-1.8984159292	0.0308628550	3.0805131513

pypyph.ch3.HTFA.TFA.
Gas phase Energy: -1923.50721856068 hartrees
Solvation Energy: -1923.51907435372 hartrees
Zero Point Energy: 210.238 kcal/mol
Coordinates:

Ir1	-0.0381013605	1.0017169031	0.3827116510
C2	-3.5255546927	3.2756291571	-1.7632552244
C3	-3.6644584633	2.9062978909	-0.4247416933
C4	-2.6246235764	2.2197027035	0.1986056131
N5	-1.5033724668	1.9183490287	-0.5063474615
C6	-1.3305532553	2.2679219170	-1.8153580915
C7	-2.3640001581	2.9607899867	-2.4583584276

H8	-4.3259385434	3.8148949683	-2.2601047943
H9	-4.5633033469	3.1586854087	0.1238220263
H10	-2.2469430994	3.2511865026	-3.4957215827
C11	-2.3990530838	0.9116101468	4.2186920199
C12	-1.3839653924	0.7212002660	3.2861100507
N13	-1.4815288464	1.1429433519	2.0185834419
C14	-2.6106430485	1.7815813852	1.6093752232
C15	-3.6687738663	1.9992123574	2.4941962008
C16	-3.5615364208	1.5638312029	3.8114604603
H17	-2.2743237330	0.5569742648	5.2359543886
H18	-0.4579119197	0.2175405393	3.5440475233
H19	-4.5634865613	2.5113117938	2.1609583092
H20	-4.3753566596	1.7339400848	4.5094368930
C21	2.4573415072	1.0210572789	-3.2408798695
C22	1.6071045103	1.6982445025	-4.1228122279
C23	0.3571496797	2.1158874553	-3.6796350387
C24	-0.0377067170	1.8587070722	-2.3570987284
C25	0.8197120372	1.1771410229	-1.4384584678
C26	2.0675429654	0.7639644149	-1.9243303946
H27	3.4342726328	0.6902702708	-3.5851724532
H28	1.9188752990	1.8956521664	-5.1439714018
H29	-0.3049063921	2.6406248445	-4.3634974566
H30	2.7531650701	0.2278222434	-1.2741018665
C31	0.6934330714	3.7164624647	1.8183463782
O32	1.2149384722	2.6774724139	1.2446679178
O33	-0.4428761571	4.1471626458	1.7143458723
C34	1.7165214290	4.4446962730	2.7291786836
F35	1.1475497316	5.4334250878	3.4300965965
F36	2.2563881327	3.5690220078	3.6145810869
F37	2.7264242593	4.9682578804	2.0085284682
O45	1.7745728801	0.3728422133	1.6675754521
H46	1.9800795672	1.3699038893	1.7548910975
C47	2.8606897389	-0.4236267812	1.6420782051
O48	3.9888348834	-0.0627283489	1.8261148856
F49	3.4800720266	-2.7012147014	1.6980453744
C50	2.4732286664	-1.8931326117	1.3664461828
F51	1.3864942586	-2.2431562865	2.0804366032
F52	2.1967315329	-2.0582754440	0.0615495697
C46	-0.8923718604	-0.8290201655	-0.1371552271
H47	-0.4967313802	-1.2174664833	-1.0794309575
H48	-0.6752049737	-1.5510801034	0.6585071840
H49	-1.9832810285	-0.7496184954	-0.2297386726

pypyph.ch3.TFA-nochel.
Gas phase Energy: -1396.71651132557 hartrees
Solvation Energy: -1396.73356490722 hartrees
Zero Point Energy: 185.453 kcal/mol
Coordinates:

Ir1	-0.2829140876	1.5906901339	0.0872405698
C2	-4.3589480234	2.0124956050	-2.2422517352
C3	-4.3777824905	1.8172423988	-0.8600687061
C4	-3.1638621351	1.6937936108	-0.1827577436
N5	-1.9971836226	1.7661431740	-0.8737035933
C6	-1.9436374508	1.9623816041	-2.2248602620
C7	-3.1490243661	2.0874512854	-2.9266042191
H8	-5.2940810730	2.1087019445	-2.7852321739
H9	-5.3186170772	1.7627945367	-0.3257185856
H10	-3.1329244257	2.2414746648	-3.9993782606
C11	-2.5023823199	1.1714193281	3.9751062085
C12	-1.4779157530	1.2676102114	3.0385400209
N13	-1.7156976563	1.4334748527	1.7292787569
C14	-3.0009011977	1.5035135623	1.2776473215
C15	-4.0723807373	1.4115637899	2.1704180733
C16	-3.8218252208	1.2455517576	3.5296135540
H17	-2.2653223510	1.0390512801	5.0251468359

H18	-0.4300798129	1.2083070580	3.3168187089
H19	-5.0920698017	1.4685745022	1.8081014039
H20	-4.6476742527	1.1737496921	4.2306237786
C21	2.0817025930	2.1224368297	-3.5644131497
C22	1.0578655513	2.2926204743	-4.5040030820
C23	-0.2694264148	2.2412476831	-4.0918717844
C24	-0.5731491101	2.0216531904	-2.7391228246
C25	0.4617976036	1.8538137130	-1.7636163622
C26	1.7868288098	1.9041556198	-2.2172555066
H27	3.1190624529	2.1607361248	-3.8885899561
H28	1.2972962616	2.4629181072	-5.5496144744
H29	-1.0622212943	2.3738211033	-4.8243716693
H30	2.5970575080	1.7722403083	-1.5063998065
C31	2.1457630494	2.4592555156	1.6567348263
O32	1.4711733500	1.4491878887	1.2145342096
O33	3.1005956707	2.4439618598	2.4128700227
C34	1.7082906589	3.8638548556	1.1355359038
F35	1.8778525801	4.8181142276	2.0516867057
F36	2.3849598507	4.2079012384	0.0284560546
F37	0.3592715491	3.9069730794	0.7893049505
C38	-0.3694730770	-0.4469408309	-0.2034664755
H39	0.5376347937	-0.8486712944	0.2576098949
H40	-1.2537406738	-0.8709784214	0.2858365477
H41	-0.3882259577	-0.7055809903	-1.2653334871

pypyph.TFA-chel.ch3.
Gas phase Energy: -1396.72911394369 hartrees
Solvation Energy: -1396.74150232141 hartrees
Zero Point Energy: 185.675 kcal/mol
Coordinates:

Ir1	-0.1248352801	1.6210674051	0.3478799648
C2	-4.0616669155	2.2018952665	-2.1679565612
C3	-4.1545744694	2.0074352855	-0.7887178617
C4	-2.9800178157	1.8384356421	-0.0537703061
N5	-1.7777540229	1.8671386189	-0.6855038958
C6	-1.6520889224	2.0586203001	-2.0339888540
C7	-2.8174511914	2.2295986594	-2.7914800700
H8	-4.9646343872	2.3327601390	-2.7561990806
H9	-5.1214305955	1.9872110520	-0.3013325539
H10	-2.7431698105	2.3810697781	-3.8621915737
C11	-2.5389841892	1.3012313680	4.1260944694
C12	-1.4686026848	1.3566426686	3.2393582749
N13	-1.6344075318	1.5211031598	1.9183890262
C14	-2.8942074877	1.6419757017	1.4091935378
C15	-4.0105009257	1.5936706078	2.2491956772
C16	-3.8327513650	1.4210759981	3.6182466529
H17	-2.3571225989	1.1655212102	5.1866581423
H18	-0.4397273444	1.2657199650	3.5730146024
H19	-5.0078258992	1.6910576502	1.8362318841
H20	-4.6933697795	1.3812948617	4.2787771770
C21	2.4325995138	2.0516705391	-3.1823363098
C22	1.4624495191	2.2630446343	-4.1704204224
C23	0.1163863304	2.2671706983	-3.8224976182
C24	-0.2603213757	2.0615708879	-2.4852548484
C25	0.7183825863	1.8516911633	-1.4623730980
C26	2.0650142537	1.8477373751	-1.8513979489
H27	3.4847399478	2.0463278786	-3.4577129817
H28	1.7583669291	2.4224522682	-5.2032589127
H29	-0.6341121733	2.4321629110	-4.5916007177
H30	2.8334361967	1.6812153676	-1.1010824470
C31	1.7091876158	2.8646869187	1.7085838223
O32	1.6799192771	1.6030923581	1.5305693045
O33	0.8393316160	3.6321182349	1.2422848476
C34	2.8467705224	3.4187447254	2.5822249132
F35	2.9563416568	4.7477149797	2.4669774284

F36	2.5999412103	3.1302244644	3.8804742074
F37	4.0259177414	2.8655278632	2.2525783634
C38	-0.3063911954	-0.4144787513	0.0040924704
H39	0.6249364584	-0.8751640591	0.3510851955
H40	-1.1467102748	-0.8374303338	0.5682602279
H41	-0.4421904556	-0.6522609413	-1.0558205590

OHM-TS

Ir1	-0.0259844092	0.0099003988	0.1464362152
H2	0.4841343671	-0.3321777580	2.9040250447
O3	3.1678816666	-0.0263391348	0.9857639081
C4	2.6410460457	1.0762777952	0.9446896078
C5	3.3942387181	2.3147700339	1.4943544700
O6	1.4547124751	1.4093227873	0.5605009063
F7	3.3540604702	3.3557796300	0.6438742890
F8	2.8095359019	2.7101550457	2.6526084666
F9	4.6771277758	2.0393704777	1.7599544424
C10	1.5283989036	-4.3101648809	-1.7930808522
C11	0.2090242606	-4.0549320056	-1.4243264430
C12	-0.1118173559	-2.8157513606	-0.8689864518
N13	0.8414665060	-1.8613748347	-0.6837873343
C14	2.1151430918	-2.1118345591	-1.0180805202
C15	2.4931473634	-3.3302435569	-1.5841694537
H16	1.7939658618	-5.2645859345	-2.2377193073
H17	-0.5597693269	-4.8017217344	-1.5826137485
H18	2.8131093526	-1.3106404411	-0.8157453249
H19	3.5311444106	-3.4914759119	-1.8528749881
C20	-3.7745755289	3.0195299198	0.7909230953
C21	-3.9272612154	1.6462978246	0.6249832991
C22	-2.7969858925	0.8336879323	0.4511820024
C23	-1.5046260297	1.4217482054	0.4511858583
C24	-1.3602974525	2.7965654577	0.6148711689
C25	-2.4977565898	3.5918007328	0.7746387475
H26	-4.6498598063	3.6478134841	0.9248442663
H27	-4.9243500950	1.2150418020	0.6151083607
H28	-0.3644282237	3.2270615143	0.6246863909
H29	-2.3867480819	4.6659668469	0.8962112480
C30	-3.8368892249	-2.7878196816	-0.1028883641
C31	-3.9755809301	-1.4402677011	0.2134923896
C32	-2.8507449554	-0.6072031500	0.1926448774
N33	-1.6403795842	-1.1535114123	-0.1109759425
C34	-1.4895330799	-2.4453457442	-0.4795516970
C35	-2.5923706471	-3.3006254425	-0.4718984167
H36	-4.7027471375	-3.4419595165	-0.0752668033
H37	-4.9439170910	-1.0328353528	0.4780644972
H38	-2.4852851240	-4.3446114413	-0.7374989962
C39	1.1137049075	0.7924337234	-2.5122502607
O40	-0.0244244978	0.6624600924	-1.9106651836
C41	1.0145213197	1.3883636069	-3.9439285198
F42	1.4830531288	2.6532066334	-3.9458953964
F43	1.7801120329	0.6686632127	-4.7898377660
F44	-0.2328816628	1.4093238348	-4.4448405670
O45	2.2411005271	0.5154618588	-2.1267908653
C46	0.3667380730	-0.9872691477	2.0380387819
H47	-0.5080240277	0.5617196521	1.5284231765
H48	-0.4216373421	-1.7152232539	2.2413885034
H49	1.3254690618	-1.4670140850	1.8518320612